PB82-166976

Compendium on Low and Non-Waste Technology
Monographs 1-20

Economic Commission for Europe (UN)
Geneva (Switzerland)

Prepared for

Environmental Protection Agency
Washington, DC

Feb 82

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-166976

NATIONS UNIES

**COMMISSION ÉCONOMIQUE
POUR L'EUROPE**

ОБЪЕДИНЕННЫЕ НАЦИИ

**ЭКОНОМИЧЕСКАЯ КОМИССИЯ
ДЛЯ ЕВРОПЫ**

UNITED NATIONS

**ECONOMIC COMMISSION
FOR EUROPE**

Télégrammes : UNATIONS, GENÈVE
Télex : 28 96 96
Téléphone : 34 60 11 31 02 11

Palais des Nations
CH-1211 GENÈVE 10

COMPENDIUM
ON
LOW-AND NON-WASTE
TECHNOLOGY
MONOGRAPHS 1-20

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO. PB82 - 166976
4. TITLE AND SUBTITLE Compendium on Low and Non-Waste Technology Monographs 1-20		5. REPORT DATE February 1982 6. PERFORMING ORGANIZATION CODE 054163
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO. ECE/ENV/36
9. PERFORMING ORGANIZATION NAME AND ADDRESS United Nations Economic Commission for Europe Palais de Nations Geneva, Switzerland		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency 401 M Street, S.W. Washington, D.C. 20460		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPAWPS

15. SUPPLEMENTARY NOTES

Related to PB81 242190 Compendium on Low and Non-Waste Technology, Vol 1 Summaries of Monographs 1-20. Some monographs are in French and Russian.

16. ABSTRACT

The monographs contain descriptions of process technologies which reduce or eliminate wastes and reduce energy usage. The low and non-waste technologies are described and compared to the conventional technologies that have been replaced. These monographs have been prepared as part of a United Nations Economic Commission for Europe (UNECE) program to promote low and non-waste technology.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Resource Recovery Resource Conservation Waste Reduction		

18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (9-73)

ATTENTION

AS NOTED IN THE NTIS ANNOUNCEMENT, PORTIONS OF THIS REPORT ARE NOT LEGIBLE. HOWEVER, IT IS THE BEST REPRODUCTION AVAILABLE FROM THE COPY SENT TO NTIS.

1a

E

NATIONS UNIES

CONSEIL
ECONOMIQUE
ET SOCIAL

RESTREINT

ENV/WP.2/5/Add.1
27 Mai 1981

FRANCAIS SEULEMENT

COMMISSION ÉCONOMIQUE POUR L'EUROPE

CONSEILLERS DES GOUVERNEMENTS DES PAYS DE
LA CEE POUR LES PROBLEMES DE L'ENVIRONNEMENT

Groupe de travail des techniques peu
polluantes et sans déchets et de la
réutilisation et du recyclage des déchets

RECUEIL SUR LES TECHNIQUES PEU POLLUANTES OU SANS DECHETS

Monographie

UTILISATION DE DECHETS DE CARRIERES ET DE VERRE USAGE

transmis par le Gouvernement de la Belgique

1. Industrie

CITI No. 3699 - Fabrication de produits minéraux non métalliques non classées ailleurs. 1/

2. Caractéristiques essentielles du procédé de fabrication

Broyage des déchets de carrières ou du verre à recycler. Production de pâte par mélange de résine polyester aux charges. Dépôt de la pâte en moules à température ambiante. Après vibration les éléments en forme sortent finis du moule en deux heures.

3. Technique de fabrication classique

1) déchets de carrières: remblai,

2) déchets de verre: recyclage dans l'industrie du verre.

1/ Classification internationale type, par industrie, de toutes les branches d'activités économiques (ENV/WP.2/5, Annexe).

4. Description de la technique de fabrication classique

Le groisil ou calcin est du verre concassé prêt pour le recyclage. Il constitue un des composants pour la fabrication du verre, remplaçant dans le four de fusion une partie de l'apport de sable et de soude. Le groisil est utilisé à concurrence d'environ 15%.

En outre, l'apport de groisil permet de réaliser une économie de 2,5% d'énergie par tranche de 10% de verre recyclé utilisé.

5. Technique nouvelle

Procédé de fabrication mis au point avec la collaboration technique de l'Institut national des industries extractives (INIEX).

1) Connu sous le nom de "MARBRE 9" en ce qui concerne le recyclage des déchets de carrières. La phase industrielle de cette technique de production est en train de démarrer.

2) En ce qui concerne l'utilisation du verre, des essais satisfaisants ont été réalisés et une unité-pilote est actuellement en voie de réalisation.

6. Description de technique de fabrication peu polluantes ou sans déchets

6.1 Description des opérations et des procédés aux divers stades du processus de fabrication

Le béton de résine se compose de charges minérales (marbre, quartz, silice, verre, etc.) réduites en diverses granulations liées entre elles au moyen de résine polyester.

Le schéma de l'unité de production est le suivant:

Stockage
Pesage des matières
Dosage

Stockage des moules

Préparation des moules

Projection de Gelcoat

Malaxage des matières

Pigmentation

Polymérisation du Gelcoat

Moulage

Polymérisation

Démoulage

Nettoyage des moules

Post-polymérisation

Parachèvement

Emballage - Stockage - Expédition des produits finis

Ces grandes étapes se décomposent elles-mêmes en un certain nombre de tâches qui demandent, dans plusieurs cas, beaucoup de soin de la part de ceux qui les exécutent.

La préparation du moule est l'étape au cours de laquelle la surface du moule, destinée à entrer en contact avec la matière, reçoit un agent de démoulage.

La projection de Gelcoat consiste en l'application d'une résine de surface sur les parois du moule; cette opération a pour but de donner à la matière un aspect parfaitement lisse. Les propriétés du Gelcoat permettent au produit de résister aux effets des intempéries et de l'ensoleillement.

Le dosage des matières dans la cuve du malaxeur est l'un des stades déterminants de la fabrication. Aussi, le respect des proportions qui définissent la compostion du matériau doit-il être rigoureux.

Le malaxage des charges minérales, de la résine synthétique et de ses adjuvants doit, en outre, s'opérer dans des conditions déterminées de température et d'humidité du milieu ambiant; les tolérances d'erreur sont ici extrêmement faibles.

La pigmentation du mélange ainsi obtenu a pour but de conférer à la matière l'aspect demandé.

Le moulage de la pâte s'effectue par répartition manuelle du mélange dans le moule; pour compléter et parfaire la répartition, on applique sur le moule un dispositif conçu suivant le principe de la transmission d'ondes vibratoires.

La polymérisation consiste en une réaction chimique destinée à assurer la solidification de la matière.

Le démoulage est réalisé par simple retournement ou par extraction de l'élément moulé.

La post-polymérisation correspond à la poursuite et l'accomplissement total de la réaction chimique. Celle-ci est accélérée grâce à l'élévation de la temperature ambiante du lieu de polymérisation.

Une finition particulière est donnée, le cas échéant, au produit. Une aire de parachèvement est prévue à cet effet.

Caractéristiques du produit - Voir annexe.

Utilisations possibles -

Elles sont extrêmement variées :

- construction : éléments de façades, revêtement muraux intérieurs et extérieurs, escaliers, dalles de sol, éléments de décoration, etc.
- sanitaire : éviers, baignoires, douches, etc.
- mobilier urbain : aubettes, abris autobus, bacs à papiers, etc.
- mobilier : tablettes de fenêtres, tablettes de radiateurs, etc.
- sculptures, etc.

6.2 Besoins en matières et en énergie par tonne de produit fabriqué

- charge minérales : 850 kgs
- résines polyester : 130 kgs
- matières diverses : 20 kgs
- eau : négligeable
- énergie : 3 GJ

6.3. Spécification de la forme et de la quantité de rejets dans l'atmosphère et dans l'eau et des rejets solides produits en cours de fabrication

Pas de rejet conséquent à l'extérieur.

- Emanations de styrène (présent dans les résines). Ces émanations ne sont pas actuellement considérées comme gênantes pour les travailleurs par le service de médecine du travail.

- Lors de la finition, un peu de poussières. Celles-ci peuvent facilement être captées par une hotte aspirante.

6.4 Spécification des normes applicables aux rejets dans l'atmosphère et dans l'eau, et aux rejets de déchets solides dans le pays ou la zone fournissant les informations

—

6.5 Spécification des mesures (complémentaires) de lutte contre la pollution nécessaires pour satisfaire aux normes en vigueur

- poussières : aspiration

- styrène : aspiration

6.6 Spécification des rejets dans l'atmosphère, dans l'eau et des rejets de déchets solides dans l'environnement

—

6.7 Données sur les coûts, destinées à permettre la comparaison des techniques peu polluantes ou sans déchets avec les techniques classiques

Produit : béton de résine et marbres synthétiques

Capacité de l'installation de production : 5 T/jour

Production annuelle : 1125 T

Capital : 1.166.667 $ des Etats-Unis

Jours ouvrables/an : 225

Lieu d'implantation : Belgique

Années de référence pour le calcul des coûts : 1979

Eléments du coût	Unités utilisées pour le calcul des coûts	Coût du facteur à l'unité en $EU*	Unités nécessaires par tonne de produit fabriqué	Coût par tonne de produit fabriqué
DEPENSES VARIABLES				
Matières premières				
- charges	kg	0,13	850	110,5
- résines	kg	1,66	130	215,8
- divers	kg	3,33	20	66,6
Energie				
- production	GJ	10	1	10
- chauffage	GJ	10	2	20
Eau	m^3	négligeable		
Main-d'oeuvre	heures-homme	10	28,8	288
Dépenses diverses (frais d'atelier et moules)	forfait	-	-	166,66
TOTAL DES DEPENSES VARIABLES				877,56
FRAIS FIXES (Administration, frais de vente et charges financières)	150% du coût de la main-d'oeuvre	15	28,8	432
Amortissement	10% du capital fixe			103,7
TOTAL PRIX REVIENT				1.413,26

* 1 $ des Etats-Unis = 30 FB.

7. Comparaison schématique de la technique classique et de la technique peu polluante ou sans déchets

Caractéristiques à comparer	Technique classique	Technique peu polluante ou sans déchets Prod. annuelle : 1125 T
Matières et énergie	- marbres et pierres de qualité: 10 GJ par tonne de produits finis - sables, soude, etc. + énergie importante	cfr. tableau p.6
Production de déchets	- 30% en marbres et pierres	presque nul
Mesures antipollution	- bacs de décantation et aménagement de remblais	pas de pollution extérieure
Rejets de déchets	Schlams	nul
Investissement et coûts de production	8.333.333 $EU*	Inv. 1.666.667 $EU* Coût de prod. : cfr. tableau p.6
Autres caractéristiques à comparer Pour des éléments de formes et fonctions égales, les poids sont d'un rapport de	5	1

* 1 $ des Etats-Unis = 30 FB.

8. Détermination des travaux de R-D nécessaires pour la mise au point de techniques peu polluantes ou sans déchets

Traitement et broyage du verre, formulations, contrôles

9. Organisme fournissant les informations

- MINERAL PRODUCTS S.A., avenue du Bois, 31 - 4920 EMBOURG (B)
- Institut National des Industries Extractives (INIEX) - Section des Polymères, rue du Chera à 4000 Liège (B)

10. Date du rapport

3 décembre 1979

8<

ANNEXE

"MARBRE 9" - MINERAL PRODUCTS S.A.

Caractéristiques du produit

1. Résistance à la flexion (kg/cm^2) : 357,2.

2. Résistance à la compression (kg/cm^2) : 714,1.

3. Résistance aux chocs :

   boule de 1 kg : pas de rupture sous la hauteur de chute de 2,20 m.

4. Usure (mm) : après 1.000 m : 1,61

   après 2.000 m : 2,99

   après 3.000 m : 4,97

5. Gélivité : aucune trace visible de dégradation

6. Absorption d'eau à température ambiante (%) : 0,56

7. Conductivité thermique (kcal/m h °C) : 0,273

8. Résistance aux acides et aux agents chimiques :

Agents	avec Gelcoat	sans Gelcoat
Vinaigre	-	faible attaque
Acide chlorhydrique 10%	-	faible attaque
Acide nitrique 10%	-	faible attaque
Acide sulfurique 10%	-	attaque franche
Ammoniaque	-	-
Huile de table	-	-
Huile minérale	-	-
Huile diesel	-	-
Essence	-	-
Kérosène	-	-
Soude à 10%	Perte de brillant	faible attaque
Détergent	-	-
Eau de Javel (pure)	-	-

9. Indice de réaction au feu suivant le projet NBN 713.030 : nul.

10. Tenue de la tonalité en exposition solaire :

après 1.000 heures d'exposition dans le Xénotest : aucune variation dans le ton (teinte examinée : verte).

Les caractéristiques 1 à 9 ont été déterminées par les laboratoires OREX (Office de contrôle et de recherches expérimentales concernant l'art de construire), 17 rue du Mail, 1050 Bruxelles, suivant les procédures d'essais NBN 224 et 319 (rapport 120.346, réf. 5339/FD/ER, 21 juin 1971).

Les caractéristiques 9 et 10 ont été déterminées dans les laboratoires de l'INIEX, rue du Chera, 4000 Liège (rapport 997, 5 juin 1973).

11. Application de divers vernis et peintures et nettoiement (tests réalisés par l'INIEX réf. 26/76 - lettre du 6 avril 1976).

Matériau testé : six plaques de "MARBRE 9" de 2 x 25 x 174 cm, dont cinq revêtues de Gelcoat.

Produits appliqués : voir liste dans le tableau des résultats, suivant une gamme complète d'échantillons sélectionnée et fournie par l'Institut communal des arts décoratifs et industriels de la ville de Liège.

Date des essais : mars 1976.

Réalisation des essais : Six plages de 4 x 11 cm ont été délimitées sur la largeur des plaques de "MARBRE 9".

Plage I : pas d'application

Plages II à VI : application du produit à tester

La plage II sert de témoin et les quatre restantes sont réservées aux essais de nettoiement. Les solvants suivants ont été expérimentés : acétone, méthanol, benzène, chlorure de méthylène. Le nettoiement a été réalisé à l'aide de chiffons imbibés de solvant dans un délai de trois à huit jours après l'application.

Résultats

a) Essais sur plaques avec Gelcoat : Le tableau ci-après résume les résultats. La signification des symboles est la suivante :

+ : Enlèvement facile, sans altération.

++ : Enlèvement après insistance; parfois léger ternissement.

+++ : Enlèvement difficile; souvent dépolissage.

0 : Sans effet.

Echantillons		Solvants				Remarques
No.	Nature	Acétone	Méthanol	Benzène	Chlorure de méthylène	
1	Vernis mat bâtiment	+	++	++	+++	
2	Vernis brillant teinté	+	++	++	+++	
3	Vernis pour métaux	+	++	++	+++	
4	Vernis satiné bâtiment	+	0	0	+++	(a)
5	Email acrylique carrosserie	+	+	+	+	
6	Email mat bâtiment	0	0	0	0	(b)
7	Email brillant bâtim.	++	0	+++	++	
8	Email satiné bâtiment	++	0	+++	++	
9	Email synth. carros.	+	++	++	+	
10	Peinture tableaux	++	++	+++	++	
11	Peinture huile	++	0	+++	++	
12	Peinture aluminium	+	0	+	+	
13	Latex extérieur	+	+	+	+	
14	Latex intérieur	Enlèvement à l'eau savonneuse				
15	Primer PVC	+	+++	+	+	
16	Primer chromate de plomb	+	+++	++	+	
17	Primer chromate de zinc	+	+++	++	+	
18	Primer neutre carrosserie	+	+++	+++	+	
19	Wash primer carros.	+	++	++	+	
20	Wash primer bâtiment	+	+	+	+	
21	Surfacer bâtiment	0	0	0	0	(c)
22	Détrempé lavable	+	+	+	+	
23	Minium fer et plomb	0	0	0	0	(c)
24	Liquide pour lustrage carrosserie	+	+	+	+	
25	Bouches-pores à la brosse	++	0	0	+	
26	Pâte abrasive pour carrosserie	Enlèvement au chiffon sec				
27	Fongicide teinté	+	+++	+++	+	

Remarques :

a) Après 3 jours d'application : enlèvement facile à l'acétone.
Après 8 jours les solvants organiques sont sans effet; nécessité d'utiliser l'acide nitrique et la spatule : le Gelcoat n'est pas attaqué.

b) Aucun solvant organique ne s'est révélé efficace. Nécessité d'imprégner d'abord à l'acide nitrique et de traiter ensuite au chlorure de méthylène : le Gelcoat n'est pas attaqué.

c) Enlèvement à l'acide chlorhydrique à 5% et à la spatule : le Gelcoat n'est pas attaqué.

L'acétone et le chlorure de méthylène donnent les meilleurs résultats. Dans les cas où un léger ternissement ou un dépolissage sont visibles, l'application de cire ou un simple traitement compound/cire permettent de retrouver l'état initial.

b) Essais sur plaques sans Gelcoat : Les produits s'enlevant le moins facilement à l'acétone et au chlorure de méthylène en présence de Gelcoat ont été appliqués sur des plaques de "MARBRE 9" non revêtues de Gelcoat :

4 : Vernis satiné bâtiment
6 : Email mat bâtiment
7 : Email brillant bâtiment
9 : Email satiné bâtiment
10 : Peinture tableaux
11 : Peinture huile
21 : Surfacer bâtiment
23 : Minium fer et plomb.

Dans tous les cas, l'enlèvement a été facile à l'acétone et au chlorure de méthylène, même pour le vernis satiné après huit jours.

c) Divers : En dehors des essais de tenue de vernis et peintures, une plaque avec Gelcoat a été imprégnée par les produits suivants :

White spirit - thinner synthétique - thinner acrylique - huile de lin - siccatif - catalyseur pour wash primer carrosserie - catalyseur pour wash primer bâtiment.

Après plusieurs jours d'imprégnation, aucune altération du Gelcoat n'a été observée.

12. Résistance à l'arrachement des ancrages.

Des essais satisfaisants ont également réalisés dans les laboratoires de l'INIEX.

Ces tests ont été réalisés sur le matériau fabriqué à base de marbre ou d'autres pierres. Les mesures sont sensiblement les mêmes dans le cas du verre.

NATIONS UNIES

CONSEIL
ECONOMIQUE
ET SOCIAL

RESTREINT
ENV/WP.2/5/Add.2
27 Mai 1981
FRANCAIS SEULEMENT

COMMISSION ÉCONOMIQUE POUR L'EUROPE

CONSEILLERS DES GOUVERNEMENTS DES PAYS DE
LA CEE POUR LES PROBLEMES DE L'ENVIRONNEMENT

Groupe de travail des techniques peu
polluantes et sans déchets et de la
réutilisation et du recyclage des déchets

RECUEIL SUR LES TECHNIQUES PEU POLLUANTES OU SANS DECHETS

Monographie

RECUPERATION DE DECHETS PLASTIQUES MELANGES

transmis par le Gouvernement de la Belgique

1. Industrie

CITI No. 3560 - Fabrication d'ouvrage en matière plastique, non classée ailleurs. 1/

2. Caractéristiques essentielles du procédé de fabrication

Récupération et réutilisation des matières plastiques mélangées après extraction de l'ordure urbaine (soit par tri automatique, soit par collecte sélective) par broyage primaire, lavage-séchage, broyage fin, plastification, granulation.

3 et 4. Technique de fabrication classique et description

Classiquement, il était impossible de recycler les plastiques mélangés. Seul le recyclage des plastiques homogènes d'une seule famille était possible.

Il n'y a donc pas de comparaison possible avec la situation classique. On peut cependant signaler que normalement l'élimination finale des déchets plastiques soit par épandage contrôlé, soit par incinération représente un non-sens sur le plan écologique et énergétique.

1/ Classification internationale type, par industrie, de toutes les branches d'activités économiques (ENV/WP.2/5, Annexe).

En effet, les plastiques sont non-biodégradables et dans les techniques d'incinération, ils créent des problèmes de fumées. (Par exemple, pollution et corrosion par HCL.)

Tous les additifs utilisés dans la formulation des matières plastiques peuvent se retrouver sous forme de fumées ou de poussières toxiques (métaux lourds par exemple).

D'un point de vue énergétique, il est dommage de brûler, après une durée de vie très courte, une macromolécule à haut contenu énergétique.

5. Technique nouvelle

La plastification FN à vis courte et les équipements amonts de prétraitement constituent un module "clef sur porte" complet qui est actuellement commercialisé. Une machine pilote fonctionne depuis deux ans au CRIF (Centre de recherche scientifique et technique de l'industrie des fabrications métalliques).

6. Description de la technique de fabrication peu polluante ou sans déchets

6.1 Description du processus de fabrication

- collecte des déchets urbains
- séparation de la fraction plastique soit sur tri automatique, soit par collecte sélective du verre et du plastique mélangé
- séparation du verre et du plastique sur verticyclone
- broyage grossier du plastique
- lavage et séchage
- broyage fin
- plastification et fabrication de l'émulsion sur la plastification à vis courte
- granulation
- mise en sac
- le granulé fabriqué peut être remis en oeuvre sur les techniques classiques de transformation des matières plastiques (injection, extrusion, etc.)

6.2 Spécification des besoins en énergie et en matière exprimés en BF/tonne de produit fabriqué et en unités physiques

électricité	1.350 FB/T	682 Kwh/T
gaz naturel (séchage)	540 FB/T	333.000 Kcal/T
eau (lavage)	60 FB/T	10 m^3/T
déchet de base	400 FB/T	1.000 kg/T

(1 $ des Etats-Unis = 30 FB)

6.3 Spécification des formes de rejets

Néant : pas de rejets extérieurs.

6.4 Spécification des normes applicables aux rejets

Les normes belges sont respectées (rejet en rivière) pour ce qui concerne les eaux de lavage du plastique.

6.5 Spécification des mesures (complémentaires) de lutte contre la pollution

Pas de rejets importants.

6.6 Spécification des rejets

Néant sauf pour l'eau : normes belges.

6.7 Données sur les coûts

Bilan des coûts de fabrication en FB/kg de granulé recyclé :

salaires	3,28 FB/kg;	5,5 heures ouvriers/tonne
électricité	1,85 FB/kg;	682 Kwh/T
gaz	0,54 FB/kg;	833.000 Kcal/tonne
eau	0,06 FB/kg;	10 m^3/tonne
amortissement	2,00 FB/kg	
frais financier	1,66 FB/kg	
recherche et maintenance	0,42 FB/kg	
collecte des déchets	0,40 FB/kg	
TOTAL	10,22 FB/kg	

7. Comparaison entre la technique classique et la technique peu polluante

7.1 Economie d'énergie et de matière

En recyclant un kilo de matière plastique, ou mieux en permettant de ne pas devoir produire ce kilo de plastique en partant du pétrole ou de fractions de pétrole brut (gaz, naphte, etc.), l'économie au niveau de l'approvisionnement est de 2 kg de pétrole brut plus l'énergie nécessaire à la synthèse chimique des macromolécules et à la transformation en produits finis.

Analyse des deux facteur matière et énergie

a) Matière

Des études ont montré que la composition de la phase plastique des ordures urbaines était la suivante (en Belgique) :

Polyoléfines (PE haute et basse densité) PP	50 à 60%
PVC	20 à 30%
Styréniques (P.S. - ABS, etc.)	15 à 20%
Divers (P.A. - thermodurcissables)	5%

Dès lors, la teneur en éléments polyoléfiniques et PVC varie de 70 à 90 pour cent de la fraction plastique. Or, ces polymères sont finalement produits au départ de l'éthylène qui, lui-même, peut être produit par vapocraquage à partir de naphte, de gasoil léger, de propane et d'éthane.

Le tableau suivant montre le rendement en éthylène des vapocraqueurs modernes.

Rendement du vapocraquage en fonction de la charge (haute sévérité)

i) rendements par rapport à la charge (%)

ii) rendements par rapports à l'éthylène (%)

	Ethane		Propane		Naphte		Gasoil léger	
Charge	1	2	1	2	1	2	1	2
Ethylène	76	100	42	100	30	100	26	100
Propylène	3	4	16	38	17	56,5	14	54
Butadiène	1,5	2	3	7	3,5	12,5	4	15,5
Benzène	0,5	0,7	2,5	6	7,5	2,5	6	23

D'autre part, 39 pour cent de l'éthylène est actuellement produit à partir du naphte dont le rendement en éthylène du vapocraquage n'est que de 30 pour cent.

Il est donc clair que le chiffre d'un approvisionnement de 2 kg de pétrole (ou de naphte) pour produire 1 kg de plastique est donc un minimum.

b) Energie

Les quantités d'énergie nécessaire à la production d'un kilo de matières plastiques qui sont habituellement proposées dans la littérature sont les suivantes :

Matières	Energie nécessaire Kwh/kg
Polystyrène	6,00
Polyéthylène haute densité	7,60
Polyéthylène basse densité	14,75
PVC	16,20

Etant donné que plus de 60 pour cent des plastiques sont constitués des PEbd et PVC à haute énergie nécessaire, la moyenne pondérée pessimiste donne 11,25 Kwh par kg.

En prenant le facteur de conversion suivant : 1 tonne équivalent pétrole équivaut à 4.000 Kwh, il faut donc importer 4,31 kg de pétrole pour produire 1 kg de plastique sous forme de produits finis.

Il faut noter en outre que le procédé de recyclage décrit ci-dessus ne nécessite, pour l'ensemble de l'usine capable de traiter 2.400 tonnes de déchets plastiques urbains, que 1 Kwh par kg au maximum.

7.2 Produits d'effluents

Néant sauf eaux de lavage des plastiques.

7.3 Mesures anti-pollution

Filtration des eaux de lavage.

7.4 Rejets

Néant.

7.5 Investissements nécessaires et personnel occupé

Pour une usine capable de recycler 2.400 T/an de déchets de plastiques, l'investissement total s'élève à 35 millions de francs belges, dont 10 millions pour le génie civil et les bâtiments.

L'installation occupe treize personnes et la production est effectuée en deux équipes.

La répartition du personnel est la suivante

cadre :	2
employés :	3
ouvriers :	2 x 4

8. Evolution de la R-D dans ce domaine

1. Le procedé complet sera testé avec l'aide de la CEE.

2. Une deuxième génération de machines sera construite afin de fabriquer directement des objets finis à partir des déchets mélangés.

3. La connaissance des mélanges de plastiques et des alliages de polymères sera approfondie.

9. Organisme fournissant les informations

FABRIQUE NATIONALE HERSTAL S.A.
Division equipements et services industriels
Département gestion environnement
rue Voie de Liège 33
B-4400 HERSTAL, Belgique.

Tel. : 041/64.08.00/64.84.00 - Telex : 41.223.

10. Date du rapport

25 novembre 1979.

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

RESTRICTED
ENV/WP.2/5/Add.3
25 May 1981
ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

USED LUBRICATING OIL AS A CEMENT KILN FUEL

Transmitted by the Government of Canada

1. Identification of industry

Not applicable. International Standard Industrial Classification: 3692.[1]

2. Basic characteristics of production process

Not applicable.

3. Name of conventional processing technology

Not applicable.

4. Description of conventional processing technology

Road oiling is the end use of most of the used oil picked up by waste oil collectors in North America. To date, this appears to have been economically attractive. However, a study by the EPA (USA) on one particular road found that:

(a) 70-75 per cent leaves the road by dust movement and runoff;

(b) 25-30 per cent is lost by volatilization, adhesion to vehicles and biodegradation;

(c) as little as 1 per cent remains on the road.

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5, Annex).

This study also showed that the vegetation in adjacent fields was high in metallic compounds that came from the road oil.

Used lubricating oils contain both portions of original additives and impurities acquired during service and at the time of collection. The oils are generally undesirable for road surfacing because of the content of water oil emulsifiers included in their original formulation and because of the pollutants inherent in their chemical composition. To remove possible dangerous contaminants and to improve their properties as dust suppressants, road oils would have to be treated before application. Treatment would consist of thermal dehydration, stripping to remove low flash-point materials followed by sulphuric acid contacting. These or other alternative processes would add substantially to the costs of road oiling while doing nothing to reduce the loss of a non-renewable natural resource. In these respects the use of waste oil as a dust palliative must be regarded as an unsatisfactory disposal method.

Another use of waste oil is in the form of fuel. However, when employed indiscriminately, the emission of non-combustible components in the oil makes fuel use a method subject to considerable pollution hazards.

An extensive review of experimental burning of waste oil in conventional oil-fired boilers and furnaces is provided by Skinner. In this review, an EPA summary of ten burning trials is quoted with the conclusion that, on average, about 50 per cent of the lead present in waste oil fed to a burner is emitted during normal burning periods; the balance is emitted during soot-blowing. The quantitative studies that have been reported have been confined to determining lead emissions in conventional combustion procedures.

A comparison of the present data for lead emissions with three published reports is given in table 1. The very substantial differences in the ratio Pb Out:Pb In (percentage) between the conventional burner tests and the cement plant experiment shows the potential over-all improvement in terms of environmental impact to be gained by burning in the cement kiln rather than burning in conventional oil-fired furnaces. There is also an advantage inherent in cement kiln burning that is not immediately apparent from much of the literature data. For the results shown in table 1, only on one test are the effects of soot-blowing indicated. Test No. 10 reported for the Shell Oil experiment showed over 100 per cent of the lead to be emitted during soot-blowing.

Soot-blowing is a pollution hazard of considerable importance when burning waste oils; it may be illustrated by considering the following reported incidences.

The "Shell Oil Company Wood River Refinery Waste Oil Burning Test" concluded:

> "Even though stack samples do not account for loss of more than 50 per cent of the lead during normal operations, it must be concluded that much larger amounts leave during soot-blowing operations. This is also confirmed by the absence of deposits in the boiler except in equilibrium amounts on the tubes."

Table 1. Comparison of lead emissions during waste oil burning at St. Lawrence Cement with other types of combustion

Test Location	Sample Identification	Pb (kg/hr)		Out/In (%)
		Total In	Total Out	
St. Lawrence Cement	22/4	20.4	0.006	.031
	23/4	19.1	0.006	.031
	30/4 (1)	14.5	0.004	.029
	30/4 (2)	14.5	0.005	.037
	1/5	14.5	0.008	.052
Humble, Baltimore Terminal (1)	15/8/72 (1)	0.107	0.047	44.0
	15/8/72 (2)	0.107	0.071	66.4
	18/9/72	0.103	0.073	70.5
	22/9/72	0.531	0.229	45.1
	23/9/72	0.531	0.176	33.2
	6/9/72	0.517	0.181	35.1
	8/9/72	0.415	0.192	46.4
	11/9/72	0.423	0.213	51.4
	13/9/72	0.476	0.225	47.2
	11/10/72	1.71	0.366	21.4
	17/10/72	1.41	0.333	24.0
	18/10/72	1.62	0.385	23.8
Shell Oil (8)	1	10.3	3.52	34
	2	10.3	3.40	33
	3	10.3	2.84	28
	4	7.7	1.97	26
	5	7.7	1.54	20
	6	7.7	1.82	24
	7	7.7	1.66	22
	8	4.2	2.04	49
	9	4.2	1.74	42
	10	4.2	4.41	102 a/
Northern States Power Company (coal-fired)	12/6/72	1.90	<.003	0.167

a/ Includes 3-minute soot blower operation.

The "Humble Oil and Refinery Company Waste Oil Burning Test" at Sewell's Point Terminal showed ground-level concentrations of less than 0.05 µg/m during normal operation, rising to 0.67 µg/m while soot-blowing. The soot from tubes contained 43 per cent lead.

Data from the API waste oil burning test performed at the Hawaiian Electric Company Plant in January 1974, showed that soot-blowing produced flakes of up to 3 to 5 inches in size. In the earlier waste oil burning tests at this installation, large amounts of stack deposits were flaked off and sporadically discharged from the stacks, even at full load conditions (56 MW). The analysis of these flakes showed the major components to be iron (36.5 per cent w/w), lead (4.3 per cent w/w), calcium (1.7 per cent w/w), zinc (0.4 per cent w/w) and magnesium (0.3 per cent w/w).

During these discharges, the lead emitted from the stack exceeded the lead in fuel fed to the boilers. This indicated the emission of accumulated ash and other deposits.

The manufacturing of cements in a rotary kiln never involves any operation comparable to soot-blowing and hence is not subject to the hazardous emissions concomitant with this procedure.

The use of waste oil as an additional fuel in coal-fired boilers has been less fully studied than in oil-fired systems. An experimental burn was carried out at Northern States Power Company in which some 110,000 litres of used oil was burned. Oil was fed at 587 l/hr and was computed to introduce lead at 1.831 kg/hr with 0.072 kg/hr from coal to give a total of 1.90 kg/hr. Lead emissions were monitored by isokinetic stack sampling and found to be less than 3.17 g/hr. This gives an average of 0.167 per cent of the lead input emitted during burning. The retention in this system was through lead containment in the fly-ash which was captured in the electrostatic precipitator system.

It is to be expected that bromine, zinc, phosphorus and other elements will all be substantially emitted when waste oil is burned in a conventional oil-burning system. No information is available to allow assessment of the behaviour of these elements when using waste oils in a coal-fired unit.

5. Name and state of development of low- and non-waste technology

The basic modification to the cement-making process[2/] consists solely of replacing a part of the normal No. 6 fuel oil with used lubricating oil. In summary, the effect of doing this was to save money for the operator without affecting product quality and at the same time to provide an environmentally benign method of disposing of used oil.

The actual quantities burned vary throughout the year as the availability of waste oil changes. During actual sustained test runs of several days duration, waste oil input was in the order to 40 per cent of the total fuel input.

[2/] The Appendix is a description of the conventional cement-making process.

Extensive testing was carried out on the final product and no appreciable change was discovered. In view of this factor and a cost advantage in using used oil, this plant has continued the practice over the last four years.

6. Description of low- and non-waste technology

For the used oil experiments, a prototype oil handling system (figure 4, Appendix) was built from three 45,000 litre tanks, thus allowing storage of a one-day supply of the oil. Only essential features of the system as regards kiln operation will be described; safety check valves, relief valves, etc., although present, will be ignored. Trucks delivered oil pumped through a 7.6 cm line in which were installed filters (double basket strainers, 30 mesh) into tank I. Tanks II and III are gravity fed from tank I. From either tank II or III, 5 cm lines convey the oil through a second filter to the pump. (Positive displacement triple screw pump.)

The oil is conveyed to the kiln or recirculated through 5 cm lines some sections of which are equipped with heaters. The recirculating feature whereby the oil is returned to tank I is essential since the stored oil in the tanks separates into a water layer and an oil layer. It also allows some heating of the oil by passing it through the line heaters. The amount of oil used was measured on the kiln burner floor by a target meter which could control the oil rate via a motorized flow control valve.

Normally, No. 6 (Bunker "C") fuel oil is burned using a standard Pillard "Triplex" Tube containing three separate Pillard MY-type mechanical atomization burners. During the experiment, one of the MY burners was fueled with the used lubricating oil, while the remaining two burners continued burning No. 6 fuel. Pillard recommends the use of these nozzles if burning oil in conjunction with either coal or natural gas, hence used lubricating oil could be burned in kilns other than oil-fired kilns.

During the trial burn, several problems were encountered with this sytem. The meter suddenly started showing extremely erratic results, a problem which caused severe operating difficulties on the kiln. A second problem encountered was a gradual decrease in the oil pressure after the pump and consequently in the flow rate which could be achieved.

As indicated elsewhere in this report, as the equipment was successfully used during previous trials, and had operated well during parts of this burn, the fault was not believed due to equipment. Some of the oil delivered during the experiment had a large amount of both water and particulate matter present (this also required very frequent strainer cleanings as well as long truck unloading times due to strainer plugging). It is currently believed that particulate matter caused excessive wear in the pump and a mixture of oil/water and/or particulate matter caused build-up in the meter.

It would seem that at least the high amount [illegible] ter in the oil results from handling after collection, which may also be the case for particulate matter. If so, improvement in the collection procedure could result in a better quality oil for utilization in cement kilns and possibly overcome the equipment problems noted. Severe fluctuations in the heating value of this oil due to water were noted during this experiment.

Since the requirements for road oiling are not stringent, it may be that the oil collectors could take more care of this aspect fairly easily. In any case, the quality of the oil delivered to cement plants must be carefully monitored if successful operation is to be maintained.

It is not known whether this system was replaced with a more permanent arrangement designed for routine operation.

The one plant known to be using used oil in a cement kiln is understandably reluctant to discuss their operating costs. They have no desire to encourage others in their area to compete for the supply of used oil. It is necessary then to discuss the economics of used oil in rather vague terms.

As a general rule the energy content of finished cement makes up about 25 per cent of the selling price. At a rough price of $55.00 per tonne, the output of the kiln tested would have a market value of $150,000 per day and the fuel cost would be approximately $37,500 per day. It is understood that used oil is purchased at a price equal to 80 per cent of the price of No. 6 fuel oil on an equivalent energy basis. If the fuel consists of 40 per cent used lube oil, the savings would be in the order to $3,000 per day.

7. Schematic comparison between conventional and the low- and non-waste technology

It was pointed out in section 4 that the disposal of waste oil on roads raises some environmental questions in that metallic compounds in the oil could find their way into the food chain. It is also a waste of the calorific value in the oil. Burning the oil retrieves the calorific value and to do so in a cement kiln solves the environmental problems because the pollutants are scrubbed out by the clinker. Thus, the cement kiln itself acts as a dry scrubber.

8. Identification of needs for further research and development

The result of using lube oil in a cement kiln is the disposal of a difficult material in a manner that offers attractive economic returns. There are indications that the same result might be obtained by burning used lube oil in a coal-fired furnace. In order to be effective, the ash must have characteristics that permit absorption of potential pollutants. Not every coal has this capability and more work is required in order better to understand this possibility.

It is also noted that used lube oil can be burned in lime kilns and the same net result can be expected.

Chlorinated organics can also be burned in lime kilns. Not only is heat available and an environmental problem avoided but also the chlorine is available to reduce alkalinity and thus improve product quality. Tests on this fuel have shown that no pollutants escape the system. Furthermore, the data indicate that appreciable volumes are available for disposal in kilns. It is also possible that some increase in cost could result from the need to dispose of alkali precipitator solids that result from some halogenated organics.

It is also noted that the combustible portion of municipal waste makes a useful fuel for kilns. Again the dry scrubbing action of the kiln solves the air pollution problem that could result from other modes of incineration.

Any further enquiries concerning the use of waste lubricating oil as a cement kiln fuel should be directed to the following address: Mr. D.J. Skinner, Chemicals Branch, Industry, Trade and Commerce, 5th floor East, 235 Queen Street, Ottawa, Ontario, Canada K1A 0H5.

9. Reporting organization

A.J. McIntyre
Department of the Environment
Fontaine Building
Hull
QUEBEC, Canada K1A 1C7.

10. Date of report

December 1978.

References

Skinner, D.J., "Preliminary Review of Used Lubricating Oils in Canada", Environment Canada, Economic and Technical Review, Report EPS 3-WP-74-4, Ottawa, 1974.

Berry, E.E., L.P. MacDonald and D.J. Skinner, 'Experimental Burning of Waste Oil as a Fuel in Cement Manufacture", Environment Canada, Technology Development, Report EPS 4-WP-75-1, Ottawa, 1975.

Gagan, E.W., "Air Pollution Emissions and Control Technology, Cement Industry", Environment Canada, Economic and Technical Review, Report EPS 3-AP-74-3, Ottawa, 1974.

MacDonald, L.P., D.J. Skinner, F.J. Hopton and G.H. Thomas, 'Burning Waste Chlorinated Hydrocarbons in a Cement Kiln", Environment Canada, Technology Development, Report EPS 4-WP-77-2.

Skinner, D.J., Private communication.

APPENDIX

Technological status of industry

The most common raw materials for manufacturing cement are limestone and clay or shale. The raw mix is ground finely and heated to about 1430°C in a rotary kiln to decompose the calcium carbonate and combine the calcium oxide with silica, alumina and iron to form a partly fused clinker. The clinker is then ground, usually with a small proportion of calcium sulphate (gypsum), which regulates set. Cements with special properties are produced by varying the oxide composition and also by adding small amounts of chemical agents at the clinker-grinding stage or later.

Raw materials

The raw materials for cement are chosen to supply:

(a) Lime component (calcareous)

(b) Silica component (siliceous)

(c) Alumina component (argillaceous)

(d) Iron component (ferriferous).

In Canada and the USA about 30 different raw materials are used to supply the required oxides. (Source: Encyclopaedia Britannica).

These materials must be prepared and correctly blended to give the required composition of each component in the clinker. After blending, the material is ready to feed to the kiln to produce clinker.

Clinker is manufactured by either wet or dry process methods. In the wet process, raw materials are prepared, blended and fed to the kiln as a water slurry (about 30 to 35 per cent water). In the dry process, raw materials are prepared, blended and fed to the kiln as a dry powder (about 0.5 per cent water). The procedures and the distinctions between the processes are illustrated below:

(1) Extraction (quarrying) of raw materials

Wet Process	Dry Process
(2) Size-reduction (grinding) and water addition	(2) Grinding and drying
(3) Blending	(3) Blending
(4) Burning in the kiln (drying, calcination, clinkering)	(4) Burning in the kiln (calcination, clinkering)

(5) Clinker grinding with gypsum to produce Portland cement

The kilns used are long, cylindrical, fire brick lined vessels, 2.4 to 6.1 m in diameter and 46 to 122 m long. The dry process kilns are shorter - 46 to 91 m, whereas the wet process kiln needs an additional drying zone (water removal which amounts to about 15 to 25 per cent of the length). The kilns are direct fired (a flame contacts the material) from the lower or discharge end. Due to the slope and rotation of these cylinders, the material moves from the higher elevation, the feed end, to the lower, hot discharge end. The retention time in the kiln is a function of the length, diameter, slope and speed of rotation. (See figs. 1 and 2.)

The raw meal or raw mix enters the kiln, in the wet process, as a slurry and to avoid lumping, bridging and breaching a network of heavy chains is installed inside the kilns to keep the material broken up and moving. These chains also enhance the heat transfer between the direct fired combustion gases and the material in the kiln. The hot gases flow up the kiln as a countercurrent to the downward flow of the solids. For a wet kiln, the exit gas temperature is around 260 to 310°C whereas with a dry-process kiln the exit gas temperature is around 310 to 540°C as there is no slurry water removal zone.

As the material moves down the kiln into progressively hotter zones, three distinct phenomena take place:

(a) vaporization of free water and liberation of water of crystallisation occurs;

(b) liberation of carbon dioxide from the limestone takes place, thus forming calcium oxide. This is called calcination and begins at 370°C;

(c) in the burning zone the lime combines with the silica and alumina, facilitated by the fluxing action of the alkalies and the iron oxide, to form a partially fused material called cement clinker. This is a complex mixture of such compounds as tricalcium silicate (3CaO . SiO) (C S)[a], dicalcium silicate (2CaO . SiO) (C S), tricalcium aluminate (3CaO . Al O) (C A) and tricalcium alumnate (4CaO . Al O . Fe O), (C Af). The burning, fluxing, chemical reaction zone is at 1400 to 1600°C.

The cement clinker leaves the kiln at a temperature of 1300 to 1460°C. This temperature is quickly lowered with air in what is called a "clinker cooler". For economy of fuel, part of the hot air from the cooler is fed to the kiln for secondary combustion air. The cooled clinker is very stable and may be stored for months without deterioration.

In order to regulate the setting times of the cement, gypsum (calcium sulphate) is usually added to the clinker and the mixture is ground to an extremely fine powder. The size of the particulate matter is less than 74 microns. In some specifications, the required fineness is expressed in terms of surface area per gram. The final product is then stored in large vessels called cement silos, from which it is drawn as needed for packaging and/or shipment.

---

[a] Note: C S, C S, C A and C Af are abbreviations used in the industry and are not chemical formulae.

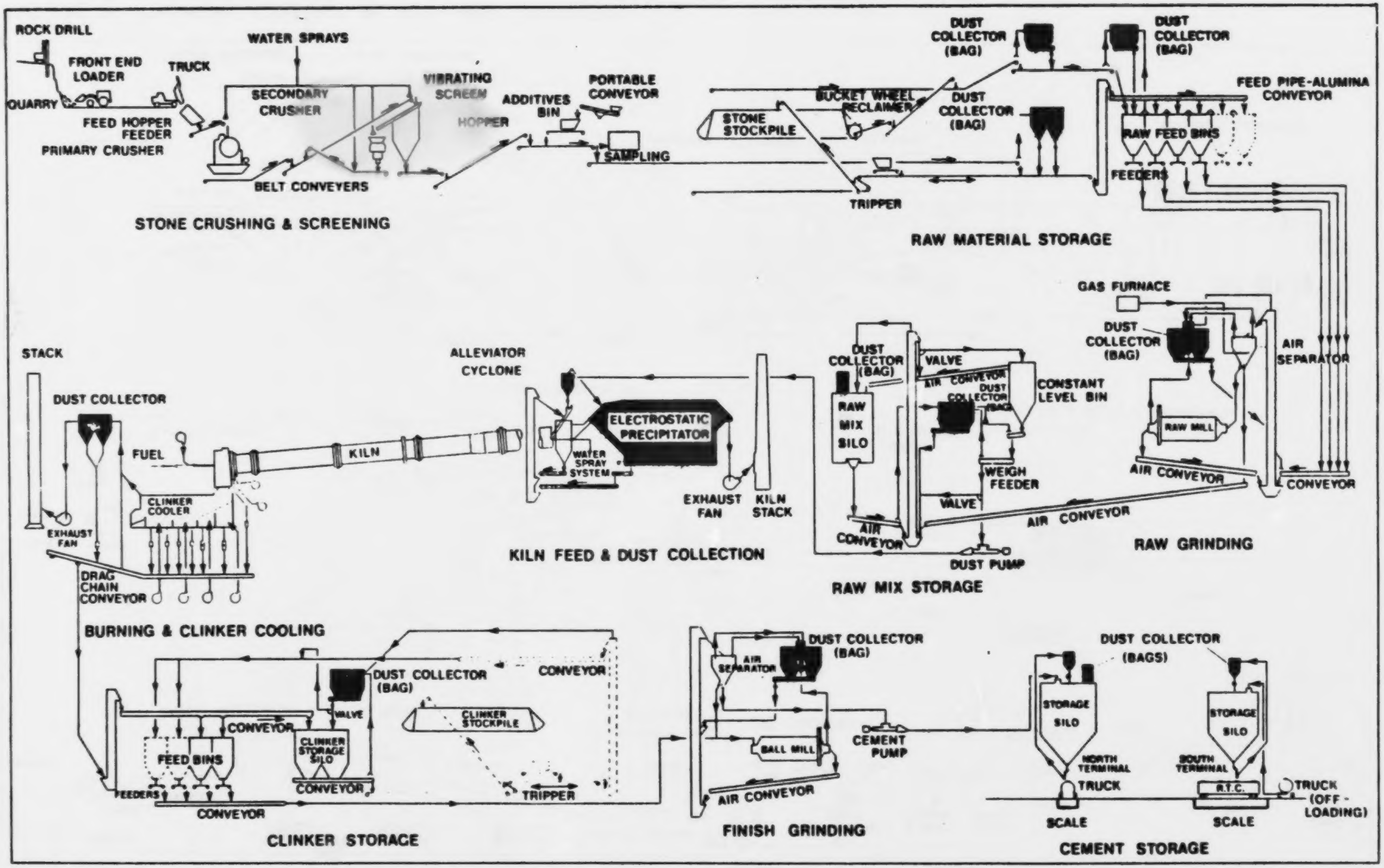

ROCK DRILL
FRONT END LOADER
TRUCK
QUARRY
FEED HOPPER FEEDER
PRIMARY CRUSHER
WATER SPRAYS
SECONDARY CRUSHER
VIBRATING SCREEN
HOPPER
BELT CONVEYERS
ADDITIVES BIN
PORTABLE CONVEYOR
SAMPLING
STONE CRUSHING & SCREENING
STONE STOCKPILE
BUCKET WHEEL RECLAIMER
TRIPPER
DUST COLLECTOR (BAG)
DUST COLLECTOR (BAG)
DUST COLLECTOR (BAG)
RAW FEED BINS
FEEDERS
FEED PIPE-ALUMINA CONVEYOR
RAW MATERIAL STORAGE
GAS FURNACE
DUST COLLECTOR (BAG)
AIR SEPARATOR
RAW MILL
AIR CONVEYOR
CONVEYOR
AIR CONVEYOR
RAW GRINDING
DUST COLLECTOR (BAG)
RAW MIX SILO
VALVE
AIR CONVEYOR
DUST COLLECTOR (BAG)
CONSTANT LEVEL BIN
WEIGH FEEDER
VALVE
AIR CONVEYOR
DUST PUMP
RAW MIX STORAGE
STACK
DUST COLLECTOR
FUEL
KILN
CLINKER COOLER
EXHAUST FAN
DRAG CHAIN CONVEYOR
BURNING & CLINKER COOLING
ALLEVIATOR CYCLONE
ELECTROSTATIC PRECIPITATOR
WATER SPRAY SYSTEM
EXHAUST FAN
KILN STACK
KILN FEED & DUST COLLECTION
DUST COLLECTOR (BAG)
VALVE
CONVEYOR
CONVEYOR
FEED BINS
CLINKER STORAGE SILO
CONVEYOR
FEEDERS
CONVEYOR
CLINKER STOCKPILE
TRIPPER
CLINKER STORAGE
DUST COLLECTOR (BAG)
AIR SEPARATOR
BALL MILL
AIR CONVEYOR
CEMENT PUMP
FINISH GRINDING
DUST COLLECTOR (BAGS)
STORAGE SILO
NORTH TERMINAL
TRUCK
SCALE
STORAGE SILO
SOUTH TERMINAL
R.T.C.
SCALE
TRUCK (OFF-LOADING)
CEMENT STORAGE

FIGURE 1 TYPICAL CEMENT PLANT - DRY PROCESS

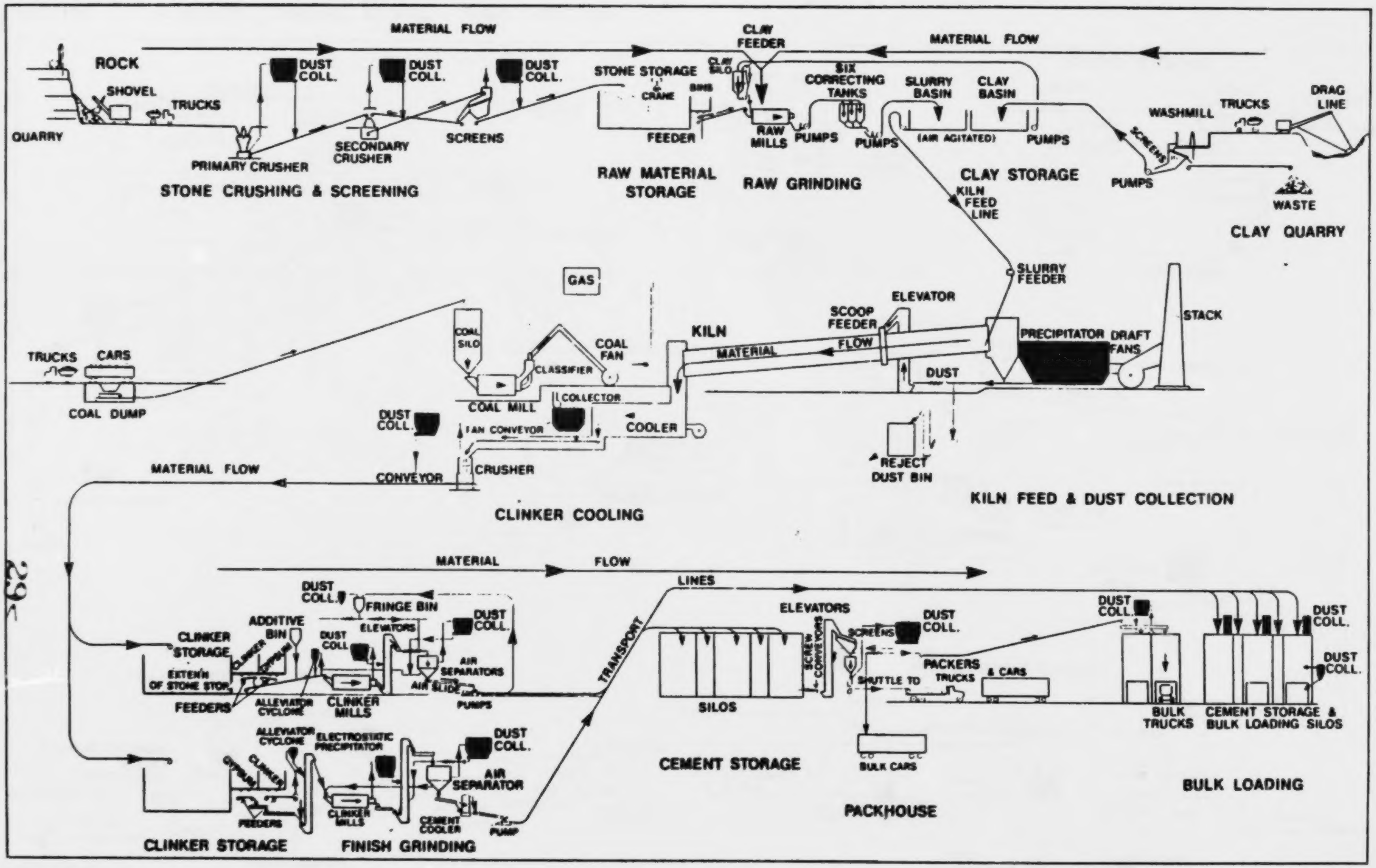

MATERIAL FLOW
ROCK
QUARRY
SHOVEL
TRUCKS
DUST COLL.
DUST COLL.
DUST COLL.
PRIMARY CRUSHER
SECONDARY CRUSHER
SCREENS
STONE CRUSHING & SCREENING
STONE STORAGE
CRANE
BINS
FEEDER
RAW MATERIAL STORAGE
CLAY FEEDER
CLAY SILO
RAW MILLS
PUMPS
RAW GRINDING
SIX CORRECTING TANKS
PUMPS
SLURRY BASIN
CLAY BASIN
(AIR AGITATED)
PUMPS
CLAY STORAGE
MATERIAL FLOW
WASHMILL
SCREENS
TRUCKS
DRAG LINE
PUMPS
WASTE
CLAY QUARRY
KILN FEED LINE
SLURRY FEEDER
GAS
TRUCKS
CARS
COAL DUMP
COAL SILO
CLASSIFIER
COAL FAN
COAL MILL
COLLECTOR
KILN
MATERIAL
FLOW
SCOOP FEEDER
ELEVATOR
PRECIPITATOR
DRAFT FANS
STACK
DUST
DUST COLL.
FAN CONVEYOR
COOLER
CONVEYOR
CRUSHER
REJECT DUST BIN
MATERIAL FLOW
CLINKER COOLING
KILN FEED & DUST COLLECTION
MATERIAL
FLOW
LINES
DUST COLL.
FRINGE BIN
ADDITIVE BIN
DUST COLL
ELEVATORS
DUST COLL.
CLINKER STORAGE
CLINKER
GYPSUM
EXTEN'N OF STONE STOR.
AIR SEPARATORS
AIR SLIDE
PUMPS
FEEDERS
ALLEVIATOR CYCLONE
CLINKER MILLS
TRANSPORT
SILOS
ELEVATORS
SCREW CONVEYORS
SCREENS
DUST COLL.
PACKERS
SHUTTLE TO
TRUCKS
& CARS
BULK CARS
DUST COLL.
BULK TRUCKS
DUST COLL.
DUST COLL.
CEMENT STORAGE & BULK LOADING SILOS
ALLEVIATOR CYCLONE
ELECTROSTATIC PRECIPITATOR
DUST COLL.
AIR SEPARATOR
GYPSUM
CLINKER
FEEDERS
CLINKER MILLS
CEMENT COOLER
PUMP
CEMENT STORAGE
PACKHOUSE
BULK LOADING
CLINKER STORAGE
FINISH GRINDING

FIGURE 2 TYPICAL CEMENT PLANT - WET PROCESS

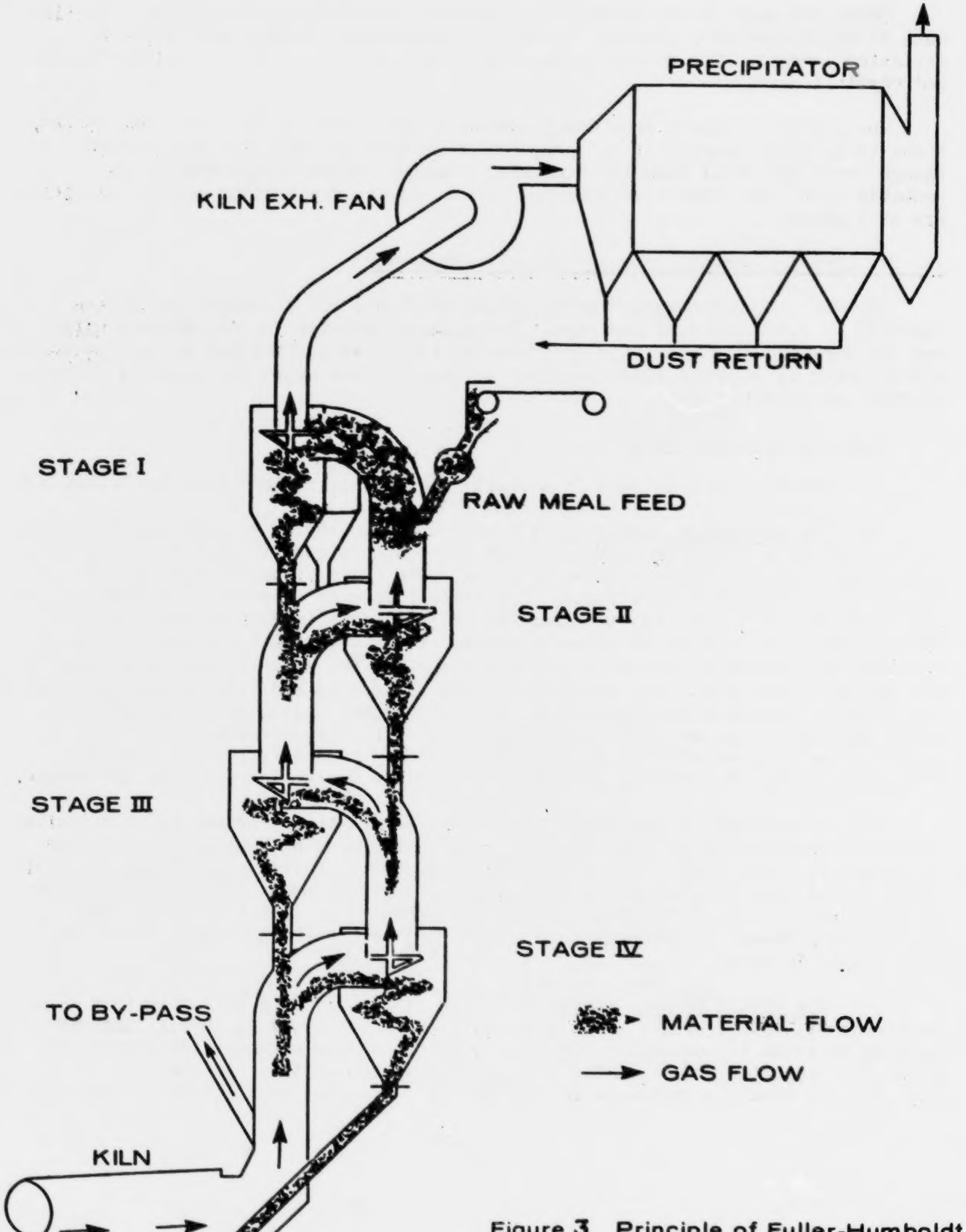

PRECIPITATOR
KILN EXH. FAN
DUST RETURN
STAGE I
RAW MEAL FEED
STAGE II
STAGE III
STAGE IV
TO BY-PASS
MATERIAL FLOW
GAS FLOW
KILN

Figure 3 Principle of Fuller-Humboldt Suspension Preheater

There are many different Portland cements each with its own special qualities, such as rapid hardening cements, low heat of hydration cements, and sulphate resisting cements. The unique properties of each are obtained by varying chemical and physical composition.

The specific example from which operating data were obtained is a dry system. There is no known example of an operation using used oil in a wet system even though there are still many in operation. Further, theory indicates it would probably work. All further discussion refers only to dry systems and the specifics are as follows:

The St. Lawrence Cement Company - Dry process system

The St. Lawrence Cement Company, Clarkson plant, has a nominal production capacity of 1,590,000 tons per year. The company operates two wet-process kilns and one dry-process kiln. This experimental trial was carried out in the dry-process system which is separate from the other process streams up to the point of clinker storage and grinding.

Relevant unit processes

(a) The kiln is a 5.2 m x 34 m Traylor unit usually fired with No. 6 fuel oil.

(b) The suspension preheater is a unit specific to dry process manufacturing. It consists of a system of cyclones, with connecting pipes, through which the hot exit-gases from the kiln are drawn by a fan. The raw meal passes through the system in a counterflow to the gas. The general flow of materials and gases in the preheater is illustrated in figure 3. Kiln feed is introduced into the duct between the first and second stage cyclones. It is swept with the hot exhaust gas into the uppermost (stage 1) cyclones where gas and material are separated. The raw feed then drops into the duct between the second and third stage cyclones and is again suspended and separated. This procedure -- being swept up with hot gases into one stage and then being dropped into the stream entering the next lowest stage - is repeated in stages 3 and 4 before the partially calcined feed enters the kiln. The average retention time of the system is less than one minute.

The raw material enters stage 1 and is preheated to approximately 350°C while the gas temperature drops from 570 to 330°C. Corresponding heat exchanges occur in stages 2, 3 and 4 such that the material enters the rotary kiln at approximately 840°C having been decarbonated to a degree up to 50 per cent. The gas temperature at the point of exit from the kiln into the preheater is 1070 to 1130°C. The St. Lawrence Cement Co. preheater is a dual Fuller-Humboldt unit with the normal four stages in each.

(c) The alkali by-pass system is an important unit in relation to this study. In common with other plants using suspension preheater systems, special measures have to be taken to reduce the build-up of chlorides and alkalies (as sodium and potassium sulphates and chlorides principally) in the system. At the St. Lawrence plant, a system is in use whereby a fraction of the kiln exhaust gases is by-passed through a conditioning tower. In the conditioning tower, water is sprayed into the gas stream to lower the temperature and condition the gases for precipitation. Concurrently, the gas velocity is reduced since the cross section of the tower is greater than that of the by-pass duct. The net effect of cooling and velocity reduction is to divide the particulate matter carried in the gas stream into two fractions. A high alkali fraction (termed by-pass dust) becomes concentrated in a material stream which is ultimately collected in an electrostatic precipitator, pelletized and discarded. A fraction of lower alkali content (termed conditioning tower solids) is returned to the raw feed silos and ultimately recycled into the raw feed stream.

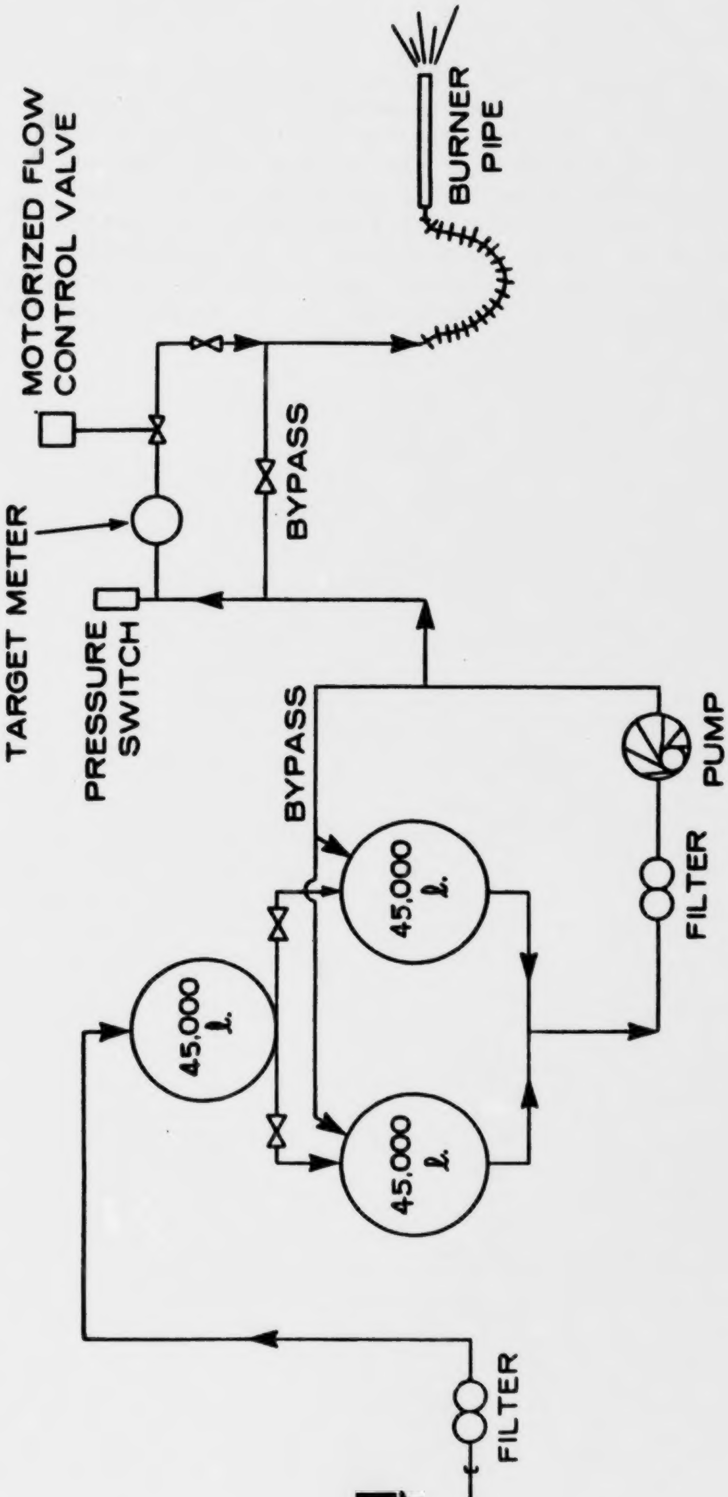

MOTORIZED FLOW CONTROL VALVE
BURNER PIPE
TARGET METER
PRESSURE SWITCH
BYPASS
BYPASS
PUMP
FILTER
45,000 l.
45,000 l.
45,000 l.
45,000 l.
FILTER

Figure 4 Waste Oil Flow Sheet

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

RESTRICTED
ENV/WP.2/5/Add.4
15 June 1981
ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste Technology and Re-utilization and Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

RETROFITTING OIL-FIRED RESIDENTIAL HEATING SYSTEMS

Transmitted by the Government of Canada

1. Identification of industry

Not applicable. International Standard Industrial Classification: 0000.[1]

2. Basic characteristics of production process

Not applicable.

3. Name of conventional processing technology

Not applicable.

4. Description of conventional processing technology

4.1 Description of the unit processes used in the production process

The components of a typical oil-fired heating unit are shown in figure 1. There are two types of oil-fired heating units in widespread use. These are: the warm air furnace which uses air as the heat transfer medium, and the boiler-burner unit which employs water as the heat transfer medium. The main differences between these two units are in the design of the heat exchangers and slight changes in the combustion chambers. However, the combustion process in each of the two types is essentially identical.

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5, Annex).

The vast majority of furnaces at present in use employ the high pressure atomizing type gun burner. The compontents of such a burner are shown in figure 2. Proper combustion is the main prerequisite for good furnace efficiency and to achieve good combustion it is first necessary to ensure that there is good air-fuel mixing. In the high pressure atomizing type burner, mixing is accomplished by pumping the fuel oil (generally No. 2 fuel oil) to a precision atomizing nozzle through which it is sprayed into the combustion chamber. The nozzle is designed and dimensioned to deliver the fuel at a specified rate and at a given pressure which is generally about 700 kpa. The fine oil spray mixes with air that is directed towards the nozzle by a fan through an air mixing tube. The air is deflected near the nozzle, creating turbulence which is conducive to good air-oil mixing. Ignition is generally accomplished by an electric spark.

The amount of air that is delivered to the combustion area is also an important parameter in achieving good combustion. If perfect mixing of the air and fuel could be achieved, the air required for complete combustion would be the stoichiometric quantity. This is the theoretical amount of air required to react with the given amount of fuel. However, since perfect mixing cannot be achieved, it is necessary to supply air in excess of the stoichiometric quantity in order to ensure complete combustion. It is common practice to express this air as the percentage of air above the theoretical requirement.

The effect of too much excess air however can result in energy losses. These "flue gas losses" occur because the increased flow rate reduces the rate of heat exchange with the result that stack temperature is increased. Thus the increased flow and higher temperature represent heat lost from the system.

4.2 Specification of materials and energy requirements per ton of output

Not applicable.

4.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the process

Air pollutants from oil fired heating units include particulate matter, oxides of sulphur and nitrogen, carbon monoxide and to a lesser extent organic compounds or hydrocarbons. The average emission factors for No. 2 heating oil are shown below in table 1.

Table 1

Particulates	0.024 g/MJ[a]
SO_2	0.44(S)[b] g/MJ
Hydrocarbons	0.015 g/MJ
Nitrogen Oxides	0.024 g/MJ
CO	0.015 g/MJ

---

[a] Note: Residential size heating units produce at the maximum 420 MJ/hr.

[b] SO_2 emissions factor is calculated by multiplying the weight per cent sulphur, (S), in the fuel by the numerical constant.

Approximately 8 per cent of the annual emissions from stationary sources in Canada can be attributed to oil-fired heating units. Though this percentage may indicate that the source is a fairly small contributor to the total emissions, there are several factors that tend to concentrate the pollutants. The first factor is that the heating season in Canada is slightly greater than half a year. Consequently, these pollutants are all emitted during the winter. Next is the fact that the majority of these heating units are situated in urban areas (approximately 80 per cent). Finally, the emissions are all exhausted at low elevations, near buildings and other structures so that natural diffusion is slow.

Particulate matter, carbon monoxide and hydrocarbons are all products of incomplete combustion. The production of these three pollutants is greatest just after the burner has turned on and just after it has shut off. During the start-up of a burner, there is a small time delay before both the air flow and the oil pressure can build up to the desired amounts. As a result, there is poor air-oil mixing and hence, incomplete combustion. Also, the low flame temperature and the cool combustion chamber at start-up create more pollutants. Similarly, the fact that shut-down cannot be attained instantaneously results in the high emissions during this period.

Emissions of oxides of sulphur, which are almost completely SO_2, are regulated by the sulphur content within the fuel. The sulphur content in No. 2 fuel is approximately 0.70 per cent by weight. Therefore, any measure that would result in using less fuel would in turn reduce the emission of SO_2.

The oxides of nitrogen that are emitted during combustion find their source in two different places. The first being atmospheric nitrogen reacting with the oxygen at elevated temperatures to produce mainly nitric oxide, NO. The second source of these nitrogen oxides is from the bonded nitrogen in the fuel. Unlike CO, particulates and hydrocarbons where there are sharp peaks in the production of these pollutants during ignition and shut-down, and relatively small amounts produced during the steady state running of the burner, NO production has an initial peak and then continues to rise as the temperature within the combustion chamber increases.

4.4 Specification of the emission standards applicable in Canada

There are no standards in Canada dealing with the emissions from residential heating units.

4.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

Not applicable.

4.6 Specification of the airborne, waterborne and solid wastes discharged into the environment

Not applicable.

4.7 Cost related data intended to permit comparison of low- and non-waste technology with conventional technology

Not available.

5. Name and state of development of low- and non-waste technology

This technology consists of specific alterations to the conventional oil-fired residential heating unit.

In response to steadily rising fuel prices, ways are being sought to reduce consumption of heating fuel by improving the efficiencies of oil burning devices. The oil-fired residential furnace, being the most widely used heating source in Canada (almost 50 per cent of all Canadian residences use oil-fired furnaces), was the subject of tests aimed at improving its efficiency. These tests were conducted in five representative Canadian homes by scientists with the Canadian Combustion Research Laboratory and these tests indicated that fuel savings could be achieved. The Federal Government has just approved a much larger scale application of the technology in Prince Edward Island in order to test the ability of the industry to make the changes and maintain the altered units.

6. Description of Low- and Non-Waste Technology

The testing done by the Canadian Combustion Research Laboratory took place over a period of two winters (1974/75 and 1975/76). The daily monitoring of fuel supply rate, total burner operating time and the number of burner cycles took place between 1 October and 13 April. This period represents over 4000 Celcius degree days (less than 18°C) with a minimum temperature of minus 30°C, an average temperature of minus 2°C and a typical total snowfall of 250 cm.

The modifications to the furnace were made to achieve two main objectives. The first was an attempt to reduce the "off cycle losses" while the second was aimed at improving the performance of the burners.

"Off cycle losses" occur in two ways. The first one being that the heat remaining in the furnace after the burner shuts off is lost up the chimney through natural convection. Secondly, warm air from the basement is convected up and out the chimney due to the gradient between its temperature and that of the outside air. The air that infiltrates into the house to replace this lost air must then be heated from the outside ambient temperature to that of the house.

One method used to reduce these losses was to reduce effectively the length of time during which the furnace was in the off cycle. This was achieved by reducing the firing rate by approximately 15 per cent, causing the furnace to run for longer periods of time. The average operation of a residential heating unit presently is one third "on" and two thirds "off". The reduced firing rate was accomplished by reducing the nozzle size. This practice cannot be taken too far or the heating system may not be able to handle the peak heating load demands even if it were to operate 100 per cent of the time. However, the furnace sizing is often greater than that required by the heating load of the home and, hence, the firing rate is higher than necessary. As a result of reducing the firing rate to reduce "off cycle losses", by making this modification it was also hoped to reduce the emissions of CO, particulates and hydrocarbons due to the less frequent start-up and shut-down phases.

The next step to reduce heat loss during the "off" cycle was to install a positive chimney damper just after the barometric damper in the flue pipe. This damper was spring-loaded and designed to return to the fully closed position 30 seconds after the burner had shut off. The purpose of this damper was to impede the convection of air up the chimney. As mentioned previously, combustion at the end of the burner cycle is not complete. Once the burner has been shut down, there is insufficient air to burn the remaining oil which results in oil-dribble. Normally, this oil-dribble would burn in the bottom of the combustion chamber after the burner has shut off and the odours would go up the chimney. However, with the positive chimney damper in place, these products have nowhere to go. Therefore, to accompany the damper, it was necessary to install a solenoid valve. Not only does the solenoid valve serve as a safety measure when used in conjunction with a positive chimney damper but it also aids in cleaner starts and shut-downs, resulting in reduced emissions. A solenoid valve is installed on the oil supply line and is essentially a time delay mechanism. During burner start-ups, the solenoid valve prevents the oil flow from beginning immediately. It allows the burner air fan to come up to speed and allows suitable oil pressure to build up before admitting the fuel to the nozzle. Similarly, for burner shut-downs, the solenoid valve cuts off the supply of oil a short time before the fan goes off, to allow more complete combustion of the remaining fuel. One further addition necessary as a safety precaution was that of a safety interlock added to the burner power circuit. With this, it was impossible for the burner to start up again unless the positive chimney damper was fully open.

In their attempt to improve the burner performance, two approaches were tried. Both of these approaches involved replacing the existing burner with one of two new, higher efficiency burners. The first burner was a prototype blue-flame burner which was being developed at the Canadian Combustion Research Laboratory and the second was a commercial, flame retention-head burner. Both burners are capable of producing a shorter, more intense flame which results in more efficient combustion.

The blue flame burner is capable of smoke-free operation at an excess air level of 25 per cent when used as a retrofit burner in an existing furnace. In such a burner, the products are partially recirculated back into the flame which produces a blue flame of relatively low temperature. The low temperature is beneficial in reducing the emissions of nitrogen oxides. A schematic diagram of the blue flame burner is shown in figure 3.

The retention head burner is equipped with a specially designed head. The air travelling through the special slots in the head is given greater turbulence and speed which enhances air-oil mixing. Retention heads are capable of operating at excess air levels which are about 25 per cent as well.

7. Schematic comparison between conventional and low- and non-waste technology

Results

All of the aforementioned modifications to the furnaces resulted in improved fuel economy and reduced emissions to some extent. Some modifications were proven to be more effective than others. The relative effectiveness of the various techniques on fuel conservation and pollutant emissions are given in table 2.

Table 2

Conservation Technique	Fuel Savings %	Emission Reduction[a/] %
Improved Burner Performance	14 - 20	28
Reduced Firing Rate	9	9
Positive Chimney Damper	3 - 9	12

[a/] Note: Each pollutant has been given equal weighting and the emission reduction is therefore the mean reductions for SO_2, CO, NO and particulates.

The effect of the reduced firing rate on the furnace performance was to decrease the furnace operating efficiency slightly (from 79.1 per cent to 78.3 per cent in one case). However, this small decrease was outweighed by the fact that the lower firing rate gave higher cyclic efficiencies. The fuel savings resulting from this furnace variation was approximately 9 per cent. Because the emissions of SO_2 and NO are dependent upon the sulphur and nitrogen content in the fuel, the reduction in these emissions (approximately 9 per cent) corresponded to the reduced fuel use. The longer burner operating times and the slight reduction in cycling frequency resulted in small reductions in CO and particulate emissions (about 14 per cent and 4 per cent, respectively). Due to the fact that hydrocarbon emissions from an oil fired furnace are considerably lower than the emissions of the other pollutants, emissions of hydrocarbons during the testing periods were not monitored.

It is important to note that there may be a considerable variation in emission levels and hence, emission savings of all types of pollutants due to the range and type of units being tested, as well as the different testing conditions used.

The installation of a positive chimney damper resulted in a fuel saving of between 3 and 9 per cent. The fuel saving with this added feature was dependent upon the external temperature and also upon the type of heating system. The positive chimney damper proved to be most effective in the test home heated by hot water. In hot water heating systems there is a continuous chimney loss by convection from surfaces whose temperatures are in the order of 60°C. Again, SO_2 and NO emission reductions were comparable to the percentage fuel saving. Seasonal emissions of CO and particulates were also reduced. These reductions were probably due to the addition of the solenoid valve.

By far the greatest fuel savings were experienced when the conventional burners were replaced by either one of the two new burners. These savings were anywhere between 14 and 20 per cent. The fuel saving with the blue flame burner was slightly smaller than that achieved by the retention-head burner. Though it did prove to offer significant fuel savings when used as a retrofit to an existing furnace, the blue flame burner was designed to perform with greatest efficiency when used in conjunction with an optimized combustion chamber. There were also major reductions in all pollutant emissions when improvements in burner performance were made. SO_2 emissions responded only to the reductions in fuel consumption whereas reductions in NO emissions were a result of both reduced fuel consumption and the decreased air level. The seasonal emissions of both CO and particulates were again reduced.

Through these tests it has been shown that significant fuel savings can be accomplished by making these modifications. The most effective technique was to improve the burner performance, followed by reduced firing rate and then by the installation of a positive chimney damper and a solenoid valve. If a home-owner were to have a complete retrofit done on the heating system, he could expect to use approximately 20 per cent less fuel than the present system operating at peak efficiency would consume.

In order to put the fuel savings into perspective, it is necessary to examine the cost of each of these various retrofitting techniques. To equip a furnace with a retention head type burner, the cost would be anywhere between $100 and $400.[1] This range is due to the fact that some existing burners require only a few alterations, while in other cases a whole new burner would be required. The reduced firing rate is accomplished by installing a smaller nozzle at the cost of about $8. A positive chimney damper, depending on the specific flue and the quality of the damper would cost in the range of $150 to $200. The solenoid valve, again depending on quality could be installed for $30 to $50. Therefore, a home-owner who has a complete retrofit done can expect to pay anywhere between $290 and $700.

To determine whether an investment somewhere in this range would provide early enough returns to the individual, he must consider the cost of his yearly heating bill. An average Canadian household with a bill of around $500 would save $100 per year and would therefore be getting returns on investment anywhere between slightly less than three years to seven years. However, for a smaller home or one that is better insulated, the period before the initial investment is returned in reduced fuel bills will be longer. This calculation was made based on the assumption that the home-owner's fuel bill would remain constant. In the actual case, however, where fuel prices are expected to continue rising, the payback period would be smaller than that stated above.

---

[1] All prices quoted are in 1979 Canadian dollars.

To look at oil-fired furnace retrofitting on a national level, the possible fuel savings are fairly substantial. Due to Canada's relatively long heating season, the consumption of domestic heating oil in Canada is fairly large. In 1976, approximately 73.5 million barrels (11.7 billion litres) of heating fuel were burned in Canadian homes. This accounts for roughly 13 per cent of Canada's total oil consumption for that year. Therefore, to reduce home heating oil consumption by 20 per cent through improved furnace efficiencies, would in turn represent a reduction in the nation's total oil consumption by 2.6 per cent. The 14.7 million barrels (2.3 billion litres) of heating oil that would be saved have a monetary value of $333.5 million at its present price to the consumer of $0.145/litre.

Any further enquiries regarding the tests that were described in this report should be directed to the following address:

Mr. R. Braaten
Canadian Combustion Research Laboratory
Energy Research Laboratories
CANMET
Department of Energy, Mines and Resources
Ottawa, Ontario
Canada.

8. Identification of needs for further research and development with regard to the low- and non-waste technology

The Prince Edward Island test, mentioned in section 5, is intended to test the support system for maintaining residential heating units. The mechanics in the trade will be trained to re-fit and adjust existing units and to provide routine maintenance. It is expected that a thousand or more units will be altered over the next year, and it will be possible to observe results on a larger scale.

9. Reporting organization

Policy Directorate
Department of the Environment
Fontaine Building
Hull, Quebec
Canada K1A 1C7

10. Date of report

August 1979

References

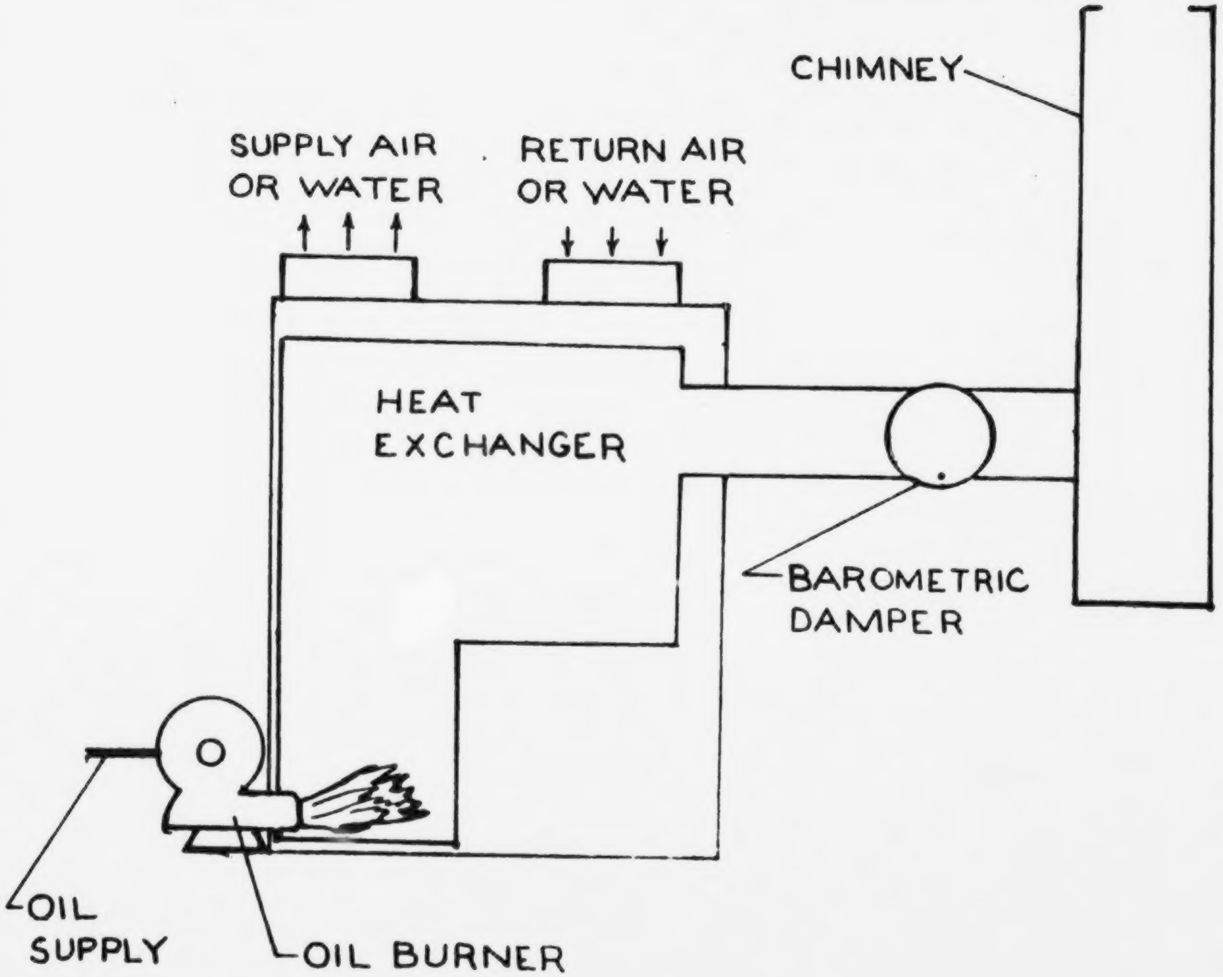
Hayden, A.C.S., R.W. Braaten, and T.D. Brown, "Emissions and Energy Conservation in Residential Oil Heating", Department of Energy, Mines and Resources, Ottawa, A.P.C.A. Journal, Vol. 28, No. 7, July 1978.

Hayden, A.C.S., R.W. Braaten, and T.D. Brown, "Oil Conservation in Home Heating", Department of Energy, Mines and Resources, Energy Research Program, Report 76-55(OP)(J), Ottawa, 1976.

ASHRAE Guide and Data Book - Equipment, George Banta Co. Inc., Menasha, Wisconsin, USA, 1972.

"State of the Art Report - Residential Heating", Environment Canada, Draft Copy, Ottawa, 1978.

FIG. 1 TYPICAL OIL-FIRED HEATING UNIT


CHIMNEY
SUPPLY AIR OR WATER
RETURN AIR OR WATER
HEAT EXCHANGER
BAROMETRIC DAMPER
OIL SUPPLY
OIL BURNER

UNITED NATIONS

ECONOMIC AND SOCIAL COUNCIL

RESTRICTED
ENV/WP.2/5/ADD.5
25 June 1981

ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-Utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

ERCO ENVIROTECH (RAPSON-REEVE) CLOSED-CYCLE TECHNOLOGY FOR BLEACHED KRAFT PULP MILLS

Transmitted by the Government of Canada

1. Identification of Industry

Pulp and paper. International Standard Industrial Classification : 3411.[1]

2. Basic Characteristics of Production Process

Wood is made up of fibres containing cellulose, hemi-cellulose and lignin. The percentage of lignin varies from 15 to 31 per cent, depending upon the wood species. About 40 to 50 per cent of the wood is a high-molecular weight polymer (alpha cellulose); the remainder is a mixture of carbohydrate polymers of lower molecular weight.

Basically, wood is pulped in three ways - chemical reaction, which dissolves a portion of the lignin; mechanical, in which fibres are separated from the whole wood mechanically; and a combination of the two, called chemi-mechanical or semi-mechanical pulping. Sulphite was once the most widely used chemical pulping process, but today the kraft process is by far the most important. In the mechanical process, logs are held against a grindstone (stone ground wood) and defibred, or chips are subjected to attrition in the disc mill to produce pulp with or without presteaming treatment (thermo-mechanical pulp, TMP; or refined mechanical pulp, RMP). The most important of the combined chemical and mechanical processes is the neutral sulphite semi-chemical (NSSC) process, in which chips are treated at high pressure and high temperature with a sodium sulphite solution and then defibred into pulp in a disc refiner.

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5.Annex).

Pulp yields vary from almost the theoretical maximum 96 per cent in the mechanical process to from 70 to 80 per cent in the chemi-mechanical process and 35 to 65 per cent in the chemical process. In the last case, yield depends upon the end-use application for the pulp; it is 33tto 35 per cent for dissolving pulp, 42 to 45 per cent for fully bleached paper-grade pulps; 48 to 58 per cent for unbleached pulp for linerboard, and 60 to 64 per cent for the high-yield bisulphite pulp used in newsprint.

3. Conventional Technology

Kraft pulping.

4. Description of Conventional Processing Technology

4.1 Description of unit operations used in the production process

Except for minor evolutionary changes, the kraft pulping process has remained the same since the commercial development of bleached kraft in the early 1930s. (However, chlorine dioxide produced a revolutionary change in pulp bleaching in the 1950s)

In the kraft process, wood chips are heated at elevated temperature and pressure (170°C top temperature, 1034 kPa pressure) with a solution of sodium hydroxide and sodium sulphide. In this cooking step, the major portion of the lignin in the wood and some of the carbohydrate materials are dissolved; the yield of unbleached pulp (the undissolved material) is around 48 per cent.

The contents of the cooking vessel are then discharged to atmospheric pressure, and the crude pulp is separated (by counter-current washing) from the solution of lignin, carbohydrate materials, and inorganic cooking chemicals. This solution (black liquor) is evaporated to 60 or 65 per cent solids and then burned in a smelting-type furnace for recovery of heat and cooking chemicals. The bottom section of the furnace is operated under reducing conditions to convert sodium sulphate to sulphide. The molten mixture of inorganic sodium carbonate and sodium sulphide flows into dissolving tanks to be dissolved in alkaline water (weak liquor) to make the so-called green liquor.

The green liquor is then treated with lime (calcium oxide) to convert the carbonate to hydroxide. The separated calcium carbonate is burned in a kiln, once again converting it to lime, and the clarified solution (white liquor) is recycled to the cooking vessel. The make-up chemical, sodium sulphate, is added with the concentrated black liquor to the furnace; alternatively, sodium hydroxide (either alone or mixed with sodium sulphide) can be added directly after the causticizing step, depending upon the desired sulphur balance of the white liquor.

The unbleached washed pulp is bleached in a multi-stage sequence. The objective of this treatment is to remove the residual lignin as well as other coloured impurities in the pulp while maintaining as much as possible of the pulp yield and pulp strength. A typical sequence (C-E-D-E-D) employs

Chlorination, caustic Extraction, chlorine Dioxide, caustic Extraction, and chlorine Dioxide, with vacuum washing after each stage. In recent modifications of this traditional bleach sequence, some chlorine dioxide replaces chlorine in the first chlorination step. These five-stage bleach sequences on softwood give a 90 to 92 per cent brightness pulp with a yield of about 44 per cent.

Counter-current flow is used in some bleach plants to decrease water consumption and effluent volume. Even with the best practice, however, substantial bleach plant liquid effluent must be treated to remove BOD and TSS.[1] Occasionally, colour and toxicity associated with such effluent must be reduced. The concentration of the dissolved solids in the bleach plant effluent is such that evaporation and burning of the collected organics are uneconomic, nor can the effluent be used in the pulp mill, as the high chloride content cannot normally be removed in the chemical recovery system.

4.2 Specification of materials and energy requirements per tonne of product

Figure 1 is a summary material and energy balance for a conventional kraft pulping process.

Table 1 summarizes the energy requirements for bleached kraft slush pulp production. Note that while the total energy requirement is 23 million kJ per tonne of slush pulp, 86 per cent of this is provided by "recovered energy" -- i.e., it is obtained by burning bark and organic materials recovered in the pulping operation. The net purchased energy is 3.3 GJ per tonne of slush pulp. Note also that the recovery and bleaching process steps are by far the most significant energy users and contributors to air emission and waste water effluents.

Table 2 summarizes the energy requirement for the manufacture of bleached kraft paper or board in an integrated pulp and paper mill. Note that pulping, bleaching, and chemical recovery again stand out as the key energy-consuming process steps. Note also that paper making, i.e. paper and board production, by itself uses half as much energy as the entire pulping operation. The 37.7 GJ per tonne represents the total energy requirement; of this, about 20 GJ is supplied by the combustion of residue fuels.

In slush pulp manufacture, most of the energy required for its manufacture is obtained from the combustion of residue fuels. Furthermore, more than 50 per cent of the total purchased energy is used in the paper making operation.

In addition to the direct use of fuels and electricity, energy is needed to produce the chemicals that are utilized in the process. For each tonne of slush pulp, the following indirect energy requirements are attributed to material flows :

---

[1] In this report : TSS = total suspended solids
TRS = total reduced sulphur
BOD = biochemical oxygen demand
BOD_5 = 5-day biochemical oxygen demand
ADT = air-dry tonnes (1000 kg)

MATERIAL	QUANTITY PER TONNE OF PULP (kg)	ENERGY REQUIREMENT PER TONNE OF MATERIAL (GJ)	"EMBODIED" ENERGY IN PRODUCING ONE TONNE OF PULP (GJ)
Cl_2	18	1.2	0.022
NaCl	19	0.57	0.011
H_2SO_4	33	0.88	0.032
$NaClO_3$	33.5	21.1	0.749
Lime	30	8.97	0.297
NaOH	35	1.2	0.042

Total per tonne = 1.15 GJ/tonne

Therefore, the total direct plus indirect energy requirement is : (23.0 GJ/tonne + 1.15 GJ/tonne = 24.15 GJ/tonne). Considering the energy that is recovered from residue fuels, the net energy requirement is 3.28 GJ/tonne + 1.15 GJ/tonne = 4.43 GJ/tonne.

4.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

Table 3 summarizes the waste-water effluent and air emissions loading for a bleached kraft pulp mill. It indicates that the main water and air emissions originate in the same process steps that are energy-intensive : pulping, recovery, and bleaching.

4.4 Specification of the emission/effluent/solid waste standards applicable in Canada

Paper mills in Canada are subject to regulations from both Federal and Provincial Governments. In general, the Federal regulations provide the minimum requirement and these are matched or slightly exceeded by Provincial agreements. Federal regulations deal only with water characteristics and for a mill of the type under discussion the requirements are as follows :

(a) Suspended solids must not exceed 11 kg/tonne (ADT)
(b) BOD must not exceed 30 kg/tonne (ADT)
(c) Toxicity must not exceed that which will allow 80 per cent of the fish that are exposed to an 80 per cent solution of the effluent to survive for at least 96 hours.

There are no Federal regulations covering gaseous or solid discharges.

4.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

Not specified.

4.6 Specification of the airborne, waterborne and solid waste discharges into the environment

Not applicable.

4.7 Cost related data intended to permit comparison of low and non-waste technology with conventional technology

Cost data for slush pulp production using a new standard kraft plant is given in Table 4.

5. Name and State of Developments of the Low and Non-Waste Processing Technology

- ERCO Envirotech (Rapson Reeve) Closed Cycle Technology for Bleached Kraft Pulp Mills.

Professors W.H. Rapson and D.W. Reeve of the University of Toronto have developed process plans for a completely effluent-free bleached kraft pulp mill. A joint venture company ERCO Envirotech Limited, was formed in 1972 to develop the concept to the mill application stage. Great Lakes Forest Products Limited (GLFP) is utilizing the results of the development work in a closed-cycle bleached kraft pulp mill at Thunder Bay, Ontario (Canada).

The first commercial installation of the Rapson-Reeve process is presently operating at Great Lakes Forest Products Limited in Thunder Bay, Ontario. The process is designed to produce none of the BOD, suspended solids, and colour that characterize effluents from the chlorine/caustic/chlorine dioxide bleaching system used with the conventional kraft process. Excess condensates from the sextuple effect black liquor evaporator are discharged, since treatment of these was not part of the mill design. (It does not affect the solid waste or air emissions, however.) The process maintains all the desirable physical characteristics of the product and reportedly can be retrofitted into existing kraft mills.

The technical/economic evaluation of the Rapson-Reeve process indicates that it would provide significant energy-and cost-savings over conventional kraft pulping and bleaching methods with effluent treatment. Further, since much of the overall waste-water effluent associated with bleached kraft pulp manufacture originates in the bleach plant, the elimination of effluents from this source would cause a major reduction in the overall waste-water effluentffrom an integrated kraft pulp and paper mill.

Should the first installation prove to be technically and economically successful, the new procdss could greatly alleviate the water pollution problems confronting a large segment of the pulp and paper industry. It might well be included in the design of all new bleached kraft pulp mills and retrofitted into existing ones.

Initial results from the first commercial installation have been published 2/ and the final evaluation should be available within one or two years to validate

---

2/ A full list of literature references on concept, development, application and initial operating results is contained in Appendix 1.

the postulated benefits of the ERCO Envirotech Closed Cycle Mill technology. If the postulated benefits are confirmed, the process could be adopted by a significant portion of the bleached kraft industry within the next decade.

6. Description of Low and Non-Waste Processing Technology

6.1 Description of the unit operations used in the production process

The closed-cycle mill concept calls for a number of changes in the conventional kraft pulping process to be made to eliminate effluents. The major ones are the following :

(a) Replacement (with chlorine dioxide) of about 70 per cent of the chlorine normally used in the first-stage chlorination step. This stage is followed by the conventional- EDED sequence of caustic extraction, chlorine dioxide, etc. Caustic addition is sufficient to combine with all the chlorine going into the bleach plant to form sodium chloride.

(b) Countercurrent washing in the bleach plant - It is possible to reduce the total amount of fresh process water into the pulp mill from 104 to 15 m^3 per tonne. Fresh water in the closed-cycle mill is used primarily for make-up to the pulp or paper machine.

(c) Re-use of all bleach-plant effluent in the pulp mill - This is utilized partly on countercurrent brown-stock washers and partly in the chemical recovery system. In this manner, all of the bleach plant chemicals and dissolved organics eventually go to the recovery furnace.

(d) Removal of sodium chloride from the white liquor (i.e., cooking liquor) - This is accomplished by evaporating the white liquor and filtring off the crystallized sodium chloride. The latter can then be used as make-up for chlorine dioxide generation and could be used as make-up for chlorate, sodium hydroxide and chloride production.

(e) Use of the effluent-free process for chlorine dioxide generation - In this procdss, the by-product sodium sulphate is crystallized from the aqueous sulphuric acid used as a reaction medium. Thus, the by-product output from the chlorine dioxide generator is solid anhydrous sodium sulphate (saltcake). A portion of this recovered saltcake can be used as make-up chemical in the kraft pulp mill; however, most of it will be sold or discarded, since production will exceed make-up demand. An alternative is to utilize hydrochloric acid to produce salt instead of saltcake. Generally, the effluent-free process is preferable to those chlorine dioxide generation processes that produce a liquid effluent which is difficult to dispose of.

(f) Making various mill process changes to facilitate closing up the water system (condensate stripping to remove methanol and mercaptan, closing up the screen room, installation of spill tanks, etc.) - As a result of these moves, somewhat larger black liquor evaporation facilities are needed to handle the intermittent return of the effluent streams from the spill tank.

6.2 Specification of Materials and Energy Requirements per tonne of output

The information obtained by ERCO Envirotech Limited was translated to a common capacity basis (250,000 tonnes per year = 725 tonnes per day). A generalized material balance is shown in Figure 2. Energy requirements are derived in table 5. The energy requirements are summarized in table 6. Indirect energy requirements associated with materials used in this process are :

MATERIAL	QUANTITY (kg)	ENERGY REQUIREMENTS (GJ)	"EMBODIED" ENERGY PER TONNE PULP (GJ)
$Cl2$	22	1.2	0.03
$NaClO_3$	61	21.1	1.29
H_2SO_4	58	0.96	0.06
NaOH	47.5	1.2	0.06
Lim	20	9.9	9.20

Total per ton = 1.64 GJ/tonne

Therefore, the total energy requirements is (21.3 GJ/tonne) + 1.64 GJ/tonne) = 22.9 GJ/tonne. Considering the energy that is recovered from residue fuels, the net energy required is 0.6 GJ/tonne + 1.64 GJ/tonne = 2.24 GJ/tonne.

6.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

A summary of pollution loads is shown in table 7.

6.4 Specification of the emission/effluent/solid waste standards applicable in Canada

See section 4-4.

6.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

None are required since the basic process provides an acceptable effluent.

6.6 Specification of the airborne, waterborne and solid waste discharges into the environment

Not applicable.

6.7 Cost related data intended to permit comparison of low and non-waste technology with conventional technology

Estimated investment and production costs for the ERCO Envirotech process are given in table 8.

7. Schematic Comparison of Conventional Kraft and Rapson-Reeve Processes

A number of advantages are expected with the Rapson-Reeve process, in addition to the minimization of water pollution. These include a higher pulp yield (about 1 per cent) better brightness stability, and better pulp strength as a result of the use of chlorine dioxide in the first stage, another yield increase due to the higher percentage of recovered fibre, lower saltcake losses, a reduction of steam consumption in the bleach plant (function of counter-current washing), and an increase in steam generation as a result of the recovered organics from the bleach plant.

ERCO Envirotech has projected that bleach-plant steam requirements will be 400 kg steam/tonne, compared with a minimum of 1,600 kg/tonne for conventional kraft pulping. Actual savings may be even higher, since conventional kraft steam requirements can be substantially higher than 1,600 kg/tonne.

Additional steam requirements for white liquor evaporation (not required for conventional kraft) are about 1,150 kg/tonne. Additional organics recovered from bleach plant effluent and burned are estimated at 68kg/tonne of bleached pulp (reclamation of 7 per cent yield loss on bleaching -- i.e. 48 per cent yield unbleached, 44.8 per cent bleached). At a fuel value of 17.4 MJ/kg and 65 per cent efficiency of heat recovery, this represents close to 400 kg steam/tonne bleached pulp. As estimated by ERCO Envirotech, this means a minimum net savings of 450 kg/tonne.

ERCO Envirotech representatives estimate that the installed cost (1975) of the salt recovery system is about $4.5 million for a 725 tonne/day mill and that the annual savings to a typical closed-cycle mill would be in the order of $2.2 million. This is broken down as follows :

	$
Steam savings	563 000
Energy recovery	414 000
Increased fibre recovery	750 000
Yield increase	750 000
Chemical increase	-1 381 000
Treatment of Effluent	1 201 000
Decreased Water Use	100 000
SRP Plant Operating Cost	- 200 000
	2 197 000

ERCO Envirotech representatives believe that problems which may arise from closing the water cycle to the maximal practical degree can be solved. They discount the possibility of problems from the build-up of trace elements in the system. In fact, Rapsom believes that there may be a positive effect from the build-up of potassium ions in the system. There will be a higher salt concentration in the white liquor than is normally found in an inland mill away from salt-water borne logs. However, ERCO Envirotech representatives point out that coastal mills normally experience a build-up of salt that is in many cases higher than in the closed cycle mill. As far as they know, there is no needdto use special construction materials in the furnaces or to redesign them to accomodate a white liquor salt content of 20 to 25 gpl. Special materials used for the first bleaching stage washer (high molubdenum alloys or titanium) are becoming industry standards.

Table 9 provides a summary comparison of unit production costs, energy use and pollution loads for the closed cycle mill and new standard kraft facilities. From this table, it appears that the ERCO Envirotech process offers a very desirable alternative technology, because it produces slush pulp at a significant cost saving, using only one-fifth the purchased direct energy and making a considerabld reduction in pollutant loads.

This comparison clearly indicates the theoretical superiority of the Rapson-Reeve process on all points. If operating experience confirms that the process performs as designed, it is reasonable to expect that it would become the chosen technology for new kraft pulping activity. In addition, it would offer a cost- and energy-effective alternative to external effluent treatment for existing kraft mills to meet effluent guidelines. It would probably receive substantial acceptance by existing mills.

8. Identification of Further Research Needs and Objectives

The Rapson-Reeve process itself does not reduce the air-borne particulates and total reduced sulphur. However, the inclusion of steam-stripping of evaporator condensates is part of the closed-cycle mill technology and is finding more application in mills. The incineration of the stripped-off TRS leads to a marked decrease in TRS emissions. Methods to decrease unwanted saltcake production or to reuse it in greater quantity are available.

9. Reporting Organization

ERCO Envirotech Ltd.
2 Gibbs Road
Islington
Ontario M9B 1R1

Attention : Mr. R.J. Read
Vice President and General Manager
Pulp and Paper Division

10. Date of Report

March 1979

APPENDIX 1

References

Rapson, W.H., "The Feasibility of Recovery of Bleach Plant Effluent to Eliminate Water Pollution by Kraft Pulp Mills". Pulp and Paper Canada 68 (12); T-635 (December 1967).

Rapson, W.H. and Douglas W. Reeve, "The Effluent-Free Bleached Kraft Pulp Mill - Part III - The Present State of Development". Tappi 56 (9), 112-115 (September 1973).

Rapson, W.H., C.B. Anderson and D.W. Reeve, "The Effluent-Free Bleached Kraft Pulp Mill - Part VI - Substantial Substitution of Chlorine Dioxide for Chlorine in the First Stage of Bleaching". Pulp and Paper Canada 78 (6), T-137 (June 1977).

Reeve, D.W., "The Effluent-Free Bleached Kraft Pulp Mill - Part VIII - Bleach Plant Renovation and Design". Pulp and Paper Canada 78 (3), T-50 - T-56 (March 1977).

Reeve, D.W., "The Effluent-Free Bleached Kraft Pulp Mill - Part VII - Sodium Chloride in Alkaline Pulping and Chemical Recovery". Pulp and Paper Canada 77 (8); T-136 (August 1976).

Reeve, D.W., J.A. Lukes, K.A. French and W.H. Rapson, "The Effluent-Free Bleached Kraft Pulp Mill - Part IV - The Salt Recovery Process". Pulp and Paper Canada 75 (8); T-293 (August 1974).

Stevens, F., "Great Lakes Pioneers Tomorrow's Technology". Pulp and Paper Canada 77 (11); pp 27-50 (November 1976).

Isbister, J.A., D.W. Reeve and W.H. Rapson, "The Closed Cycle Concept Kraft Mill at the Great Lakes Paper Company, Limited - A Status Report" presented at the PIMA International Management Conference, Minneapolis, Minn.(USA), 22 June, 1978.

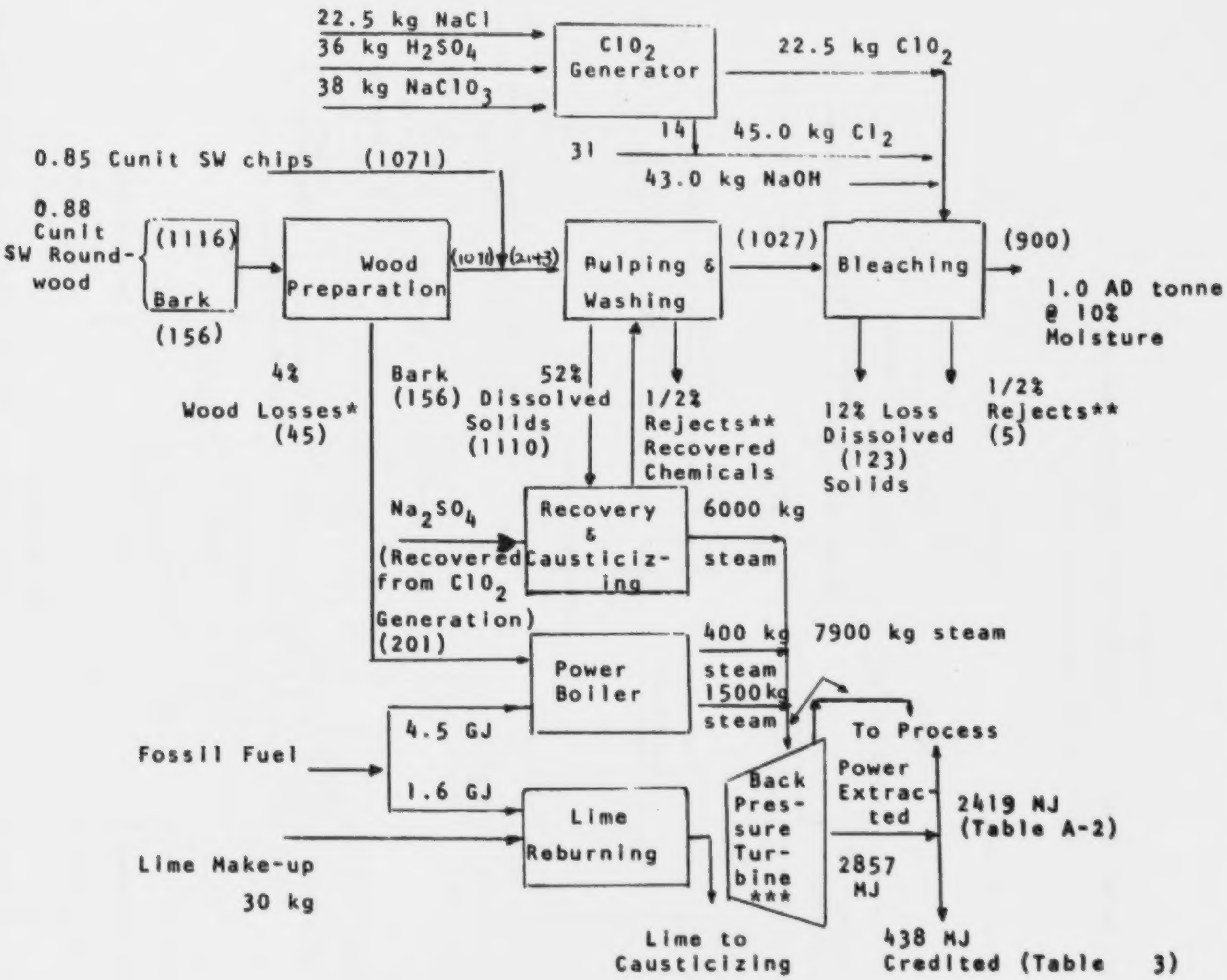
Isbister, J.A., R.G. Rae, D.W. Reeve and D.C. Pryke, "The Closed Cycle Concept Kraft Mill at the Great Lakes Paper Company, Limited - An Advanced Status Report" presented at the CPPA Environmental Improvement Conference, Thunder Bay, Ontario (Canada), (17 October, 1978).

Reeve, D.W., J.D. Kramer, G. Rowlandson and W.H. Rapson, "The Closed-Cycle Bleached Kraft Pulp Mill - 1978", presented 15 November 1978 at the TAPPI Pulping Conference, New Orleans, La.(USA).

Kramer, J.D., J.F. Cornell, D.C. Pryke and G. Rowlandson, "Spill and Effluent Control in the Closed-Cycle Mill", presented at the 1979 TAPPI Environmental Conference in Houston, Texas (USA).

Pattyson, G.W., R.G. Rae, D.W. Reeve and W.H. Rapson, "Bleaching in the Closed-Cycle Mill at Great Lakes Forest Products". Presented at the International Pulp Bleaching Conference, June 1978, Toronto, Ontario (Canada).

Figure 1- Standard Kraft Technology Material and Energy Balance (Basis: 1.0 AD Tonne Slush Pulp)


22.5 kg NaCl
36 kg H_2SO_4
38 kg $NaClO_3$
ClO_2 Generator
22.5 kg ClO_2
14
31
45.0 kg Cl_2
43.0 kg NaOH
0.85 Cunit SW chips (1071)
0.88 Cunit SW Round-wood
(1116)
Bark
(156)
Wood Preparation
(1011)
(2143)
Pulping & Washing
(1027)
Bleaching
(900)
1.0 AD tonne @ 10% Moisture
4% Wood Losses* (45)
Bark (156)
52% Dissolved Solids (1110)
1/2% Rejects** Recovered Chemicals
12% Loss Dissolved (123) Solids
1/2% Rejects** (5)
Na_2SO_4 (Recovered from ClO_2 Generation) (201)
Recovery & Causticiz-ing
6000 kg steam
400 kg steam
7900 kg steam
1500 kg steam
Power Boiler
To Process
4.5 GJ
Fossil Fuel
1.6 GJ
Lime Reburning
Lime Make-up 30 kg
Back Pres-sure Tur-bine ***
Power Extrac-ted
2857 MJ
2419 MJ (Table A-2)
Lime to Causticizing
438 MJ Credited (Table 3)

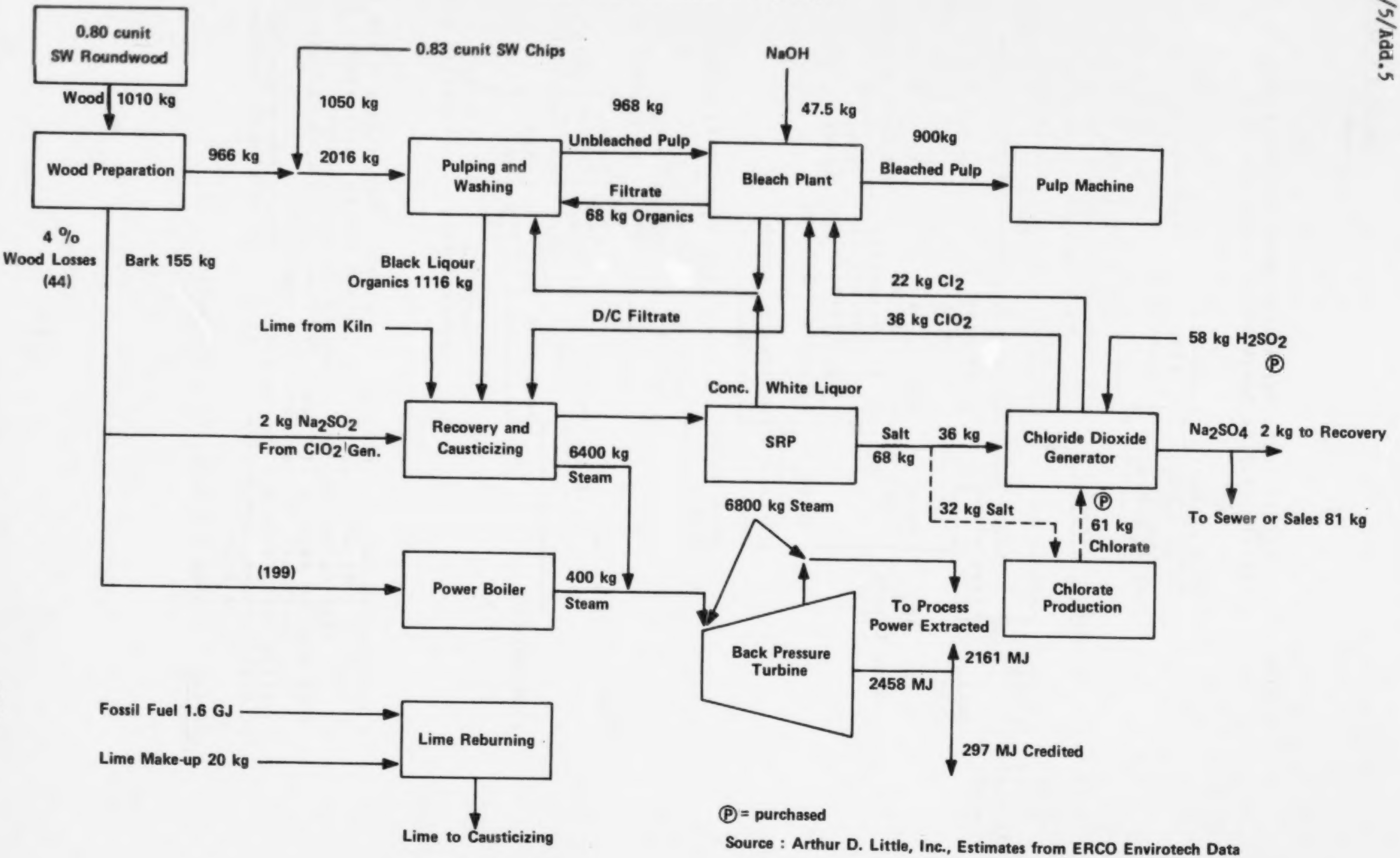
( ) Indicates bone-dry (BD) kg; 1.0 air-dry (AD) tonne = 900 BD kg
1 cunit = 2.83 m^3 of solid wood; weight per BD cunit ranges from about 1000 kg to 1500 kg, depending on wood species.
* 2% Loss on barking (suitable for fuel recovery) + 2% loss on chipping (suitable for fuel or fibre recovery).
** Fibre loss (suitable for recovery in lower-grade products).
*** Heat-to-power conversion in this type of turbine is typically about 1172 kJ/MJ.

Source: Arthur D.Little,Inc., estimates.

Figure 2

Rapson-Reeve Effluent-Free Process Material and Energy Balance

Basis: 1.0 AD tonne to Pulp Dryer


0.80 cunit SW Roundwood
Wood
1010 kg
Wood Preparation
966 kg
0.83 cunit SW Chips
1050 kg
2016 kg
4 %
Wood Losses
(44)
Bark 155 kg
Pulping and Washing
968 kg
Unbleached Pulp
Filtrate
68 kg Organics
NaOH
47.5 kg
Bleach Plant
900kg
Bleached Pulp
Pulp Machine
Black Liqour
Organics 1116 kg
D/C Filtrate
22 kg Cl2
36 kg ClO2
58 kg H2SO2
Ⓟ
Lime from Kiln
2 kg Na2SO2
From ClO2 Gen.
Recovery and Causticizing
6400 kg
Steam
Conc.
White Liquor
SRP
Salt
68 kg
36 kg
32 kg Salt
Chloride Dioxide Generator
Na2SO4
2 kg to Recovery
To Sewer or Sales 81 kg
Ⓟ
61 kg
Chlorate
Chlorate Production
6800 kg Steam
(199)
Power Boiler
400 kg
Steam
Back Pressure Turbine
To Process
Power Extracted
2161 MJ
2458 MJ
297 MJ Credited
Fossil Fuel 1.6 GJ
Lime Make-up 20 kg
Lime Reburning
Lime to Causticizing
Ⓟ = purchased

Source : Arthur D. Little, Inc., Estimates from ERCO Envirotech Data

55<

TABLE 1

ENERGY REQUIREMENTS FOR BLEACHED SLUSH PULP

(New mill basis, by process step)

	Wood Preparation	Pulping	Bleaching	Chemical recov. Liquor prep. & Lime Reburning	Misc. & Auxiliaries	Water Effluent Treatment	Total
Consumption (GJ/tonne)							
(Lime Reburning)	—	—	—	1.63	—	—	1.63
m	—	3.85	7.20	6.74	0.81	—	18.6
r	0.51	0.53	0.44	0.81	0.07	0.46	2.8
l energy	0.51	4.38	7.64	9.18	0.88	0.46	23.0
vered energy	(1.16)	—	—	(18.61)	—	—	(19.7)
purchased energy	(0.65)	4.38	7.64	(9.43)	0.88	0.46	3.2

: Arthur D. Little, Inc. estimates.

TABLE 1

ENERGY REQUIREMENTS FOR BLEACHED SLUSH PULP

(New mill basis, by process step)

	Wood Preparation	Pulping	Bleaching	Chemical recov. Liquor prep. & Lime Reburning	Misc. & Auxiliaries	Water Effluent Treatment	Total
Energy Consumption (GJ/tonne)							
Fuel (Lime Reburning)	—	—	—	1.63	—	—	1.63
Steam	—	3.85	7.20	6.74	0.81	—	18.6
Power	0.51	0.53	0.44	0.81	0.07	0.46	2.8
Total energy	0.51	4.38	7.64	9.18	0.88	0.46	23.0
Recovered energy	(1.16)	—	—	(18.61)	—	—	(19.7)
Net purchased energy	(0.65)	4.38	7.64	(9.43)	0.88	0.46	3.2

Source: Arthur D. Little, Inc. estimates.

TABLE 2

ENERGY REQUIREMENTS FOR A NEW, INTEGRATED BLEACHED KRAFT PULP MILL

(Pulp Yield = 42 percent (BD Basis)

	Steam		Power		
	kg/tonne	Equivalent GJ/tonne /	MJ/tonne	Equivalent GJ/tonne /	Total Equivalent GJ/tonne
Wood Preparation	0		436	0.51	0.51
Pulping	1250	3.85	456	0.53	4.33
Bleaching	2400	7.20	377	0.44	7.64
Chemical Recovery	1900	5.74	595	0.70	6.40
Liquor Preparation	350	1.0	99	0.12	1.12
Water Treatment and Effluent Disposal	0	—	395	0.46	0.46
Shops Stores and Miscellaneous	250	0.81	60	0.07	0.9
Lime Reburning	0	—	—	—	1.6
Total Energy Usage for Slush Pulp	6150	18.6	2419	2.83	23.0
Paper or Board Production	4250	12.8	1587	1.86	14.7
Total Energy Usage, Slush Pulp and Paper or Board	10400	31.3	4006	4.69	37.7

Recovered Heat c/

Spent liquor: 6000 kg steam/AD tonne = 18.6 GJ Ref. Table 1 Also: 16 mm BTU (ADL Report = 18.6GJ
Bark and sawdust: 400 kg steam/AD tonne = 1.16 GJ

a/ Process steam estimated at 2560 kJ/kg (steam heat content less condensate credit) and 85 percent boiler efficiency = 3024 kJ/kg steam

b/ Extracted power estimated at 1172 kJ/MJ

c/ Recovered heat based on steam at 3024 kJ fuel equivalent/kg. This represents a recovery boiler heat efficiency of 75 percent.

Source: Arthur D. Little, Inc. estimates

TABLE 3

Water Effluent Loads for Bleached Slush Pulp

(New mill basis by process step)

	Wood Preparation	Pulping	Bleaching	Chem. recovery Liquor prep. & Lime reburning	Misc. and Auxiliaries	Water Effluent Treatment	Total
ter Effluent Loads							
otal flow, (m^3/tonne)	3.79	22.7	71.9	18.9	—	—	117.3
SS (kg/tonne)	4.0	8.5	7.0	13.5	—	—	33.0
OD (kg/tonne)	1.0	11.5	15.5	5.0	—	—	33.0
olor (kg/tonne)	7.5	32.5	105	2.5	—	—	147.5
Emission loads							
articulates (kg/tonne)	0	0	—	100	—	—	100
RS (kg/tonne)	0	4.5	—	7.5	—	—	12

rce: Arthur D. Little, Inc. estimates

TABLE 3

Water Effluent Loads for Bleached Slush Pulp

(New mill basis by process step)

	Wood Preparation	Pulping	Bleaching	Chem. recovery Liquor prep. & Lime reburning	Misc. and Auxiliaries	Water Effluent Treatment
Water Effluent Loads						
Total flow, (m^3/tonne)	3.79	22.7	71.9	18.9	—	—
TSS (kg/tonne)	4.0	8.5	7.0	13.5	—	—
BOD (kg/tonne)	1.0	11.5	15.5	5.0	—	—
Color (kg/tonne)	7.5	32.5	105	2.5	—	—
Air Emission loads						
Particulates (kg/tonne)	0	0	—	100	—	—
TRS (kg/tonne)	0	4.5	—	7.5	—	—

Source: Arthur D. Little, Inc. estimates

TABLE 4

STANDARD BLEACHED KRAFT SLUSH PULP INVESTMENT AND PRODUCTION COSTS

Product: Slush Pulp   Process: Std.Bl.Kraft   Location: Southeast

By products: Turpentine, Tall Oil   Fixed Investment: \$130x10^6 Depreciation Period (yr): 16

Annual/Design Capacity 260,000 ADTonne   Working Capital: \$10 x 10^6

Annual Production: 250,000 ADTonne   Stream Days/Yr.: 345   Year used for costing purposes: 1975

A. Manufacturing Costs	Units Used in Costing or Annual Cost Basis	\$/Unit	Units Consumed per Tonne of Product	\$/ADTonne of Product
VARIABLE COSTS				
Raw Materials				
. Pulpwood	Cunits	34	1.73	58.8
. Chemicals				33.1
Byproduct Credits				
. Turpentine				
. Tall Oil				(2.2)
Energy				
. Purchased Fuel	GJ	1.80	6.1 (p.5)	11.0
. Electric Power Purch.			0	
Energy Credits				
. Electric Power	MJ	0.005	438	(2.2)
Water [b/]				
. Process (Consumption)	M	-	45.9	-
. Cooling (Circulation rate)	M	-	83.4	-
Direct.Operating & Supv. wages	Man-hr	6.1	0.77	4.7
Maintenance Labour & Supv. wages	Man-hr	7.0	0.66	4.6
Maintenance Materials & Suppl.				5.5
Labour Overhead	at 32% Direct and Maintenance Wages			3.3
Misc. Variable Costs/ Credits				
. Operating supplies				1.1

TABLE 4 (cont'd)

STANDARD BLEACHED KRAFT SLUSH PULP INVESTMENT AND PRODUCTION COSTS

FIXED COSTS

Plant Overhead	at 50% Direct and Maintenance Wages	4.4
Local Taxes and Ins.	at 2% Fixed Capital	10.40
Depreciation	at 6 ¼% Fixed Capital	32.5
TOTAL PRODUCTION COSTS		165.0
Return on Investment (pre-tax) (incl. working capital)	at 20% Total (Fixed & Working) Capital	112.0
POLLUTION CONTROL		40.2
TOTAL		315

a/ Based on manufacturing process only.

b/ The cost of supplying and treating process and cooling water are included in the details of investment and operating costs, i.e., these costs include pumps, filters, power, labour, etc., for water supply, but not effluent treatment.

B. Derivation of Fixed Capital Costs and Pollution Control Operating Costs

FIXED CAPITAL COSTS:

		$ million
Direct Manufacturing		
Manufacturing Process		125.0
OSHA		1.5
Air Control[c]		2.6
Water Control[c]		2.0
	Use	131.1
Pollution Control		
Water - Internal		2.0
Water - External		12.0
Water - Color Removal		7.0
Air		3.0
	Use	24.0

POLLUTION CONTROL OPERATING COSTS

		$/ADT
Operation and Maintenance		15.0
Depreciation @ 6 ¼%		6.0
Pretax R.O.I. @ 20%		19.2
	Use	40.2

---

[c] The amount that is economically justified, in that the value of the recovered product offsets the investment and operating cost of the installed equipment.

TABLE 5

ENERGY REQUIREMENTS FOR THE CLOSED-CYCLE MILL PROCESS FOR KRAFT SLUSH PULP, BY MAJOR PROCESS STEP

(New Mill Basis)

	Steam[a]		Power[b]		Total Energy
	(kg/AD tonne)	(GJ/tonne)	(MJ/tonne)	(GJ/tonne)	(GJ/tonne)
Wood preparation	-	-	417	0.49	0.49
Pulping	1250	3.85	456	0.53	4.38
Bleaching	400	1.2	337	0.40	1.60
Chemical Recovery	2150	6.5	635	0.74	7.24
Liquor Preparation	450	1.36	99	0.12	1.48
Salt Recovery	1150	3.5	79	0.09	3.59
Water Treatment and Effluent Disposal	-	-	79	0.09	0.09
Shops, Stores and Miscellaneous	250	0.8	59	0.07	0.87
Lime Reburning	-	-	-	-	1.60
Total Energy Usage for Slush Pulp	5650	17.2	2161	2.53	21.3

Recovered Heat [c]

Spent liquor (incl. bleach plant organics: 6400 kg steam/AD tonne = 19.5 GJ
Bark and hogged fuel: 400 kg steam/AD tonne = 1.16 GJ

a/ Process steam estimated at 2560 kJ/kg (steam heat content less condensate credit) and 85 per cent boiler efficiency = 3024 kJ/kg

b/ Extracted power estimated at 1172 kJ fuel/MJ

c/ Recovered heat based on steam at 3024 kJ fuel equivalent/kg. This represents a recovery boiler heat efficiency of 75 per cent.

Source: Arthur D. Little, Inc., estimates from ERCO Envirotech data.

TABLE 6

SUMMARY - ENERGY CONSUMPTION FOR THE CLOSED CYCLE MILL FOR KRAFT SLUSH PULP PRODUCTION, BY PROCESS STEP

(New Mill Basis)

	Wood Preparation	Pulping	Bleaching	Chemical Recovery and Liquor Preparation	Salt Recovery	Miscellaneous and Auxiliaries	Effluent Treatment	Total
y Consumption (GJ/tonne)								
e Reburning	-	-	-	1.60	-	-	-	1.6
am	-	3.85	1.16	7.86	3.5	0.8	-	17.2
er	0.49	0.53	0.40	0.86	0.09	0.07	0.09	2.5
al Energy	0.49	4.38	1.56	10.3	3.59	0.87	0.09	21.3
overed Energy c/	(1.16)	-	-	(19.5)	-	-	-	(20.7)
Purchased Energy	(0.67)	4.38	1.56	(9.2)	3.59	0.87	0.09	0.6

ce: Arthur D. Little, Inc., estimates from ERCO Envirotech data.

ee table 5.

TABLE 6

SUMMARY - ENERGY CONSUMPTION FOR THE CLOSED CYCLE MILL FOR KRAFT SLUSH PULP PRODUCTION, BY PROCESS STEP

(New Mill Basis)

	Wood Preparation	Pulping	Bleaching	Chemical Recovery and Liquor Preparation	Salt Recovery	Miscellaneous and Auxiliaries	Effluent Treatment	Total
Energy Consumption (GJ/tonne)								
Lime Reburning	-	-	-	1.60	-	-	-	1.6
Steam	-	3.85	1.16	7.86	3.5	0.8	-	17.2
Power	0.49	0.53	0.40	0.86	0.09	0.07	0.09	2.5
Total Energy	0.49	4.38	1.56	10.3	3.59	0.87	0.09	21.3
Recovered Energy c/	(1.16)	-	-	(19.5)	-	-	-	(20.7
Net Purchased Energy	(0.67)	4.38	1.56	(9.2)	3.59	0.87	0.09	0.6

Source: Arthur D. Little, Inc., estimates from ERCO Envirotech data.

c/ See table 5.

TABLE -7

SUMMARY - POLLUTION LOADS FOR THE CLOSED CYCLE MILL FOR KRAFT SLUSH PULP PRODUCTION, BY PROCESS STEP

(New Mill Basis)

	Wood Preparation	Pulping	Bleaching	Chemical Recovery and Liquor Preparation	Salt Recovery	Miscellaneous and Auxiliaries	Effluent Treatment	Total
ent Loadsa/								
w (m³/tonne)								< 15
onne)								-
/tonne)								< 5
								-
ltcake (kg/tonne)								81
ns								
tes (kg/tonne)		0		100				100
onne)b/								2

thur D. Little, Inc., estimates from ERCO Envirotech data.

effluent is low-level contaminated water from gland seals, cooling tower blowdown, etc.
water from evaporators, boilers, turbines, and chemical production is recycled through
towers. Excess saltcake is discharged or sold.

pounds are removed to a high percentage through collection, air and/or steam stripping
ineration.

TABLE 7

SUMMARY - POLLUTION LOADS FOR THE CLOSED CYCLE MILL FOR KRAFT SLUSH PULP PRODUCTION, BY PROCESS STEP

(New Mill Basis)

	Wood Preparation	Pulping	Bleaching	Chemical Recovery and Liquor Preparation	Salt Recovery	Miscellaneous and Auxiliaries	Effluent Treatment	Total
Water Effluent Loads[a]								
Total Flow (m^3/tonne)								< 15
TSS (kg/tonne)								-
BOD (kg/tonne)								< 5
Colour								-
Excess Saltcake (kg/tonne)								81
Air Emissions								
Particulates (kg/tonne)		0		100				100
TRS (kg/tonne)[b]								2

Source: Arthur D. Little, Inc., estimates from ERCO Envirotech data.

[a] Aqueous effluent is low-level contaminated water from gland seals, cooling tower blowdown, etc. Cooling water from evaporators, boilers, turbines, and chemical production is recycled through cooling towers. Excess saltcake is discharged or sold.

[b] TRS compounds are removed to a high percentage through collection, air and/or steam stripping and incineration.

TABLE 7

SUMMARY - POLLUTION LOADS FOR THE CLOSED CYCLE MILL FOR KRAFT SLUSH PULP PRODUCTION, BY PROCESS STEP

(New Mill Basis)

	Wood Preparation	Pulping	Bleaching	Chemical Recovery and Liquor Preparation	Salt Recovery	Miscellaneous and Auxiliaries	Effluent Treatment	Total
Water Effluent Loads[a]								
Total Flow (m^3/tonne)								< 15
TSS (kg/tonne)								-
BOD (kg/tonne)								< 5
Colour								-
Excess Saltcake (kg/tonne)								81
Air Emissions								
Particulates (kg/tonne)		0		100				100
TRS (kg/tonne)[b]								2

Source: Arthur D. Little, Inc., estimates from ERCO Envirotech data.

[a] Aqueous effluent is low-level contaminated water from gland seals, cooling tower blowdown, etc. Cooling water from evaporators, boilers, turbines, and chemical production is recycled through cooling towers. Excess saltcake is discharged or sold.

[b] TRS compounds are removed to a high percentage through collection, air and/or steam stripping and incineration.

TABLE 8
ERCO ENVIROTECH CLOSED-CYCLE PROCESS INVESTMENT AND PRODUCTION COSTS

Product: Slush Pulp
Byproducts: Turpentine, Tall Oil
Annual Design Capacity: 268,000 AD Tonne
Annual Prod: 250,000 AD Tonne

Process: Rapson-Reeve Effluent-Free Kraft Continuous a/
Fixed Investment: $130 x 10
Working Capital: $10 x 10
Stream Days/Yr: 345

Location: Southeast
Depreciation Period(yr): 16
Year used for costing purposes: 1975

A. Manufacturing Costs	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per tonne of Product	$/AD Tonne of Product
VARIABLE COSTS				
Raw Materials				
. Pulpwood	C units	34	1.63	56.2
. Chemicals				41.8
ByProduct Credits				
. Turpentine, Tall Oil				(2.2)
Energy				
. Purchased Fuel	GJ	1.80	1.6	2.9
. Electric Power Purch.				
Energy Credits(Specify form)				
. Electric Power	MJ	0.005	297	(1.5)
Water b/				
. Process (Consumption)				
. Cooling	M^3	-	< 15	-
Direct. Operating and Supv. Wages	Man-hr	6.1	0.9	5.5
Maintenance Labour and Supv. Wages	Man-hr	7.0	0.8	5.6
Maintenance Materials and Supp.				
Labour Overhead	at 32% Direct and Maintenance Wages			3.3
Misc. Variable Costs/Credits				
. Operating Supplies				1.1
FIXED COSTS				
Plant Overhead	at 50% Direct and Maintenance Wages			5.5
Local Taxes and Ins.	at 2% Fixed Capital			10.4
Depreciation	at 6-¼% Fixed Capital			32.5
TOTAL PRODUCTION COSTS				166.6
Return on Investment (pretax) (incl. working capital)	at 20% Total (Fixed and Working Capital)			112.0
POLLUTION CONTROL				9.45
TOTAL				288.0

---

a/ Based on manufacturing process only.

b/ The cost of supplying and treating process and cooling water are included in the details of investment and operating costs, i.e., these costs include pumps, filters, power, labour, etc., for water supply, but not effluent treatment.

TABLE 8

ERCO ENVIROTECH CLOSED-CYCLE PROCESS INVESTMENT AND PRODUCTION COSTS (CONT'D)

B. Derivation of Fixed Capital Costs and Pollution Control Operating Costs

FIXED CAPITAL COSTS:	$ Million
• Direct Manufacturing	
Manufacturing Process	125.0
OSHA	1.5
Air Control[c]	2.6
Water Control[c]	3.0
	130.0
• Pollution Control	
Water - Internal (incl. $0.5 million royalty)	6.0
Water - External	0.0
Air	3.0
	9.0
POLLUTION CONTROL OPERATING COSTS: ($9 Million)	**$/ADT**
Operation and Maintenance	1.0
Depreciation @ 6-½%	2.25
Pretax R.O.I. @ 20%	7.2
	9.45

---

[c] The amount that is economically justified, in that the value of the recovered product offsets the investment and operating cost of the installed equipment.

TABLE 9

COMPARISON OF THE ERCO ENVIROTECH PROCESS WITH STANDARD KRAFT SLUSH PULP

(New Mill Basis)

Item	Process	Standard Kraft
Plant Investment, Pollution Control ($million)	139	154
Operating Cost ($/AD/tonne) including Pollution Control	288	315
Net Purchased Energy (GJ/tonne)	0.6	3.3
Pollution Loads		
Water Volume (m /tonne)	≈ 15 a/	117.3
BOD (kg/tonne)	< 5	33
TSS (kg/tonne)	-	33
Colour (kg/tonne)	-	150
Air Emissions		
Particulates (kg/tonne)	100	100
TRS (kg/tonne)	2	12

a/ Aqueous effluent is low level contaminated water.

UNITED NATIONS
ECONOMIC AND SOCIAL COUNCIL

RESTRICTED
ENV/WP.2/5/Add.6
26 June 1981
ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW-AND NON-WASTE TECHNOLOGY

Monograph

PRESSURIZED STONE GRINDING FOR MECHANICAL PULP PRODUCTION (TAMPELLA)

Transmitted by the Government of Finland

1. Identification of Industry

Pulp and paper industry, mechanical pulping, pressurized ground wood; International Standard Industrial Classification : 3411. 1/

2. Basic characteristics of the mechanical pulping process

Basically, wood is reduced to pulp in three ways - chemical reaction, which dissolves a portion of the lignin; a mechanical process, in which wood is ground or refined to fibres; and a combination of these two called chemi-mechanical or semi-chemical. In the mechanical process there are four main production lines, stone ground wood (SGW), pressurized ground wood (PGW), refined mechanical pulp (RMP) and thermo-mechanical pulp (TMP). In the stone ground wood (SGW) and the pressurized ground wood (PGW) process, logs are held against a grindstone and in that way reduced to fibres; the yield is about 95 per cent (SGW) and 94 per cent (PGW). The refined mechanical pulp (RMP) is produced by chipping the wood and subjecting the chips to attrition in a disc mill; the yield is about 95 per cent. Thermo-mechanical pulp (TMP) is produced in the same way as RMP; the chips are, however, heated before entering the disc refiner; the yield is about 93 per cent.

Stone ground wood (SGW) has, for newsprint, traditionally been the main source of pulp. It however requires a significant addition of semibleached kraft pulp as reinforcement fibre : about 18 per cent. With thermo-mechanical pulp (TMP) for newsprint, the amount of reinforcement fibre can be substantially reduced to about 7 per cent, but the process again has a much higher power demand. The pressurized ground wood (PGW) is developed in order to reduce the amount of required reinforcement of semi-bleached kraft pulp and still get by with the low power demand, as with stone ground wood. RMP is almost comparabld to SGW but requires more energy to produce. A fibre balance for the different production methods is shown in Figure 3.

1/ International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex).

3. Name of conventional mechanical pulping processes

The traditional mechanical pulping processes used today are :

SGW = stone ground wood
TMP = thermo-mechanical pulp
RMP = refined mechanical pulp (not further dealt with in this case).

4. Description of the TMP and SGW processes

4.1 Description of the unit operations used in the TMP and SGW processes

In the TMP process, wood logs are debarked and chipped. Alternatively saw mill waste can be used as raw material. The waste is chipped and screened. The chips are fed into a pressurized preheating vessel where they are heated to about 100 to 140 °C. The preheated chips are refined in one or two stages, normally in disc refiners. Today, a conventional concept would be that the first refining stage is pressurized while the second is at atmospheric pressure. After refining, the fibre has to be conditioned in a latency removal chest of 4 per cent consistency, at about 60 °C for 20 minutes. In order to obtain the quality needed for news print production, the stock has to be bleached and screened.

In the traditional SGW process, wood logs are debarked and whole logs are held against the grindstone and reduced to fibres. The mechanical pulp produced this way has to be screened and may be somewhat bleached before it is used for newsprint preparation.

4.2 Specification of the materials and energy requirements for the TMP and SGW processes per ton of final-end product (news-print)

The materials and energy requirements are examined by selecting a newsprint mill with capacity for 500 tons of paper per day (dryness 95 per cent) as a comparison base. The mill is assumed to buy power from an external grid, in addition to the amount that may be generated as back-pressure power in connection with the steam generation for the paper machine dryer. The steam and power aspects are not dealt with in this report. The basic concept is described in the simplified flowsheet (Fig. 1).

When producing newsprint from thermo-mechanical pulp, it is assumed that the raw material is the same as for ground wood, that is, logs. The alternative, - as, for example, saw mill waste - is not considered in this comparison.

The material and energy requirements for thermo-mechanical pulp and stone ground wood for the production of 1 ton newsprint (95 per cent) are following :

	TMP	SGW
- wood, m^3 solid	2,32	2,0
- semi-bleached kraft air dried kg	74	190
- power kWh	2430	1600
- steam MJ	4200	4200

In addition, bleaching chemicals, peroxide and/or dithionite are used, depending on the quality of the newsprint. This factor (as well as chemicals that may be used for waste treatment) is not taken into account, because it does not have a significant influence on the comparison.

4.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the TMP and SGW production processes

In the production of thermo-mechanical pulp, the pulping yield is assumed to be about 93 per cent. The yield loss is mainly a waterborne waste which gives a BOD_7-load of approximately 28 kg BOD_7/ton newsprint produced.

In the production of stone ground wood pulp, the pulping yield is assumed to be about 95 per cent. The yield loss appears mainly as waterborne waste which gives a BOD_7-load of approximately 8kg BOD_7/ton newsprint produced.

4.4 Specification of the emission (effluent) solid waste standard applicable in Finland

At the time of this report, there are no emission effluent or solid waste discharge limits defined as certain numbers by law in Finland. The problems are dealt with on a case-by-case basis, individually for each mill. However, the National Water Board issues guidelines for waterborne wastes. These guidelines are given for discharge of suspended solids and oxygen consuming matter (biochemical oxygen demand).

4.5 Specification of (add-on) pollution control measures necessary for compliancoe with existing standards

For comparison, an activated sludge waste-water treatment plant is assumed in order to reduce the BOD_7-load of the recipient significantly.

4.6 Specification of the airborne, waterborne and solid waste discharge into the environment

The BOD_7-load from the TMP-process which is about 28 kg BOD_7/ton newsprint and that of the SGW-process which is about 8 kg BOD_7/ton newsprint are normally reduced in an effluent treatment plant.

Additionally, both for TMP and SGW about 2,5 per cent of the wood entering the mill ends up as barking residue; however, it is normally burned for steam and power production.

The TMP and SGW processes are not a source of any significqnt airborne waste.

The residual BOD_7-load to the recipient would be about 6 kg BOD_7/ton newsprint for TMP and about 2 kg BOD_7/ton newsprint for SGW.

4.7 Cost related data intended to permit comparison of pressurized ground-wood process with conventional thermo-mechanical pulp and stone ground-wood process for newsprint production

For the comparison of the above-mentioned processes, only those departments where the differences in investment cost are to be found are considered, when accounting for the fixed capital. This means that for TMP the chipping, the thermo-mechanical pulping and the waste-water treatment departments are considered. For the stone ground-wood pulping, the grinding and the waste-water departments are considered. The departments not included in the capital cost alculation are barking, paper machine (complete), steam and power generation and other supporting departments, as these investment costs remain approximately the same for both processes. As there will be no significant difference in the working capital requirement, this is not considered in this report. Cost data given in tables 1 and 2 are intended only to permit comparison.

5. The state of development of the pressurized ground wood (PGW) processing technology

The pressurized ground wood process is developed from the conventional hydraulic stone grinder by changing the grinder so that the processed wood is ground in a gas-tight space under pressure; the pressurized grinding has been implemented as a batch process.

Since 1976, Oy Tampella Ab of Tampere (Finland) and MoDoColl AB of Ornskoldsvik (Sweden) have, in co-operation, studied the possibilities of improving the strength properties of stone ground wood to make it meet the market requirement better than at present. Furthermore, the consumption of energy and wood material in the process has been kept as low as possible in order to spare decreasing natural resources.

Based on a preliminary study, experiments were carried out with a production scale grinder in Sweden in 1977, by altering the machine to perform when pressurized. As a result of these trial runs, mechanical pulp of quite a new type was obtained; its strength - especially tear resistance - was considerably better than that of stone ground wood, corresponding to the strength figures of thermo-mechanical pulp. Also it became evident that the energy consumption of the process was lower than that of the presently known processes for the manufacturing of similar mechanical pulp.

In 1978, a prototype unit was produced in Finland, and has been operated in order to confirm the positive results of the first trial runs in Sweden and to perfect the technique of pressurized stone grinding and the mechanical equipment. At the time of writing this report, 14 PGW units are on order for commercial operations divided between Finland, USA and the Federal Republic of Germany. The first commercial PGW units will start up in the summer of 1980.

Patents for the system are pending in Scandinavia, most European countries, North America, South America and Japan.

TABLE 1

Product :	Newsprint
By-product:	None
Plant capacity:	500 tons per day
Annual production:	170 000 tons per annum
Process:	Thermo-mechanical pulping (TMP)
Fixed capital:	19 000 000 dollars (for comparison only)
Working capital:	Not considered for comparison
Operating days/yr :	350
Location:	Scandinavia
Depreciation:	10% of fixed capital per annum
Period (yr):	10
Year used for costing purpose:	1979

TMP (for comparison only)

Cost items	Units used in costing	Factor/cost Unit	Units required per ton	Cost/ton of product
VARIABLE COSTS				
Raw materials (minus by-product credits)	m^3 solid ADT	$ 39.5/m^3s. $ 474/ADT	2.32 0.074	91.6 35.1
Energy (minus energy credits)	kWh (MJ)	$ 0.04/kWh	2430	97.2
Water	m^3	equal		
Labour				
(a) Operating	man-hr	equal		
(b) Maintenance	man-hr	equal		
overhead	% of labour cost	equal		
Miscellaneous		equal		
TOTAL VAR. COST				224.0
FIXED COSTS		-	-	-
Plant overhead	% of labour costs	equal		
Local taxes and insurance	1% of fixed capital	190 000	1/170 000	1.12
Depreciation	10% of fixed capital	1 900 000	1/170 000	11.18
TOTAL PROD. COST				236.30
Return on investment	15% of total capital	2 850 000	1/170 000	16.76
Pollution control				3.87
GRAND TOTAL				256.93

TABLE 2

Product:	Newsprint
By-products:	None
Plant capacity:	500 tons per day
Annual production:	170 000 tons per annum
Process:	Stone ground wood (SGW)
Fixed capital:	18 000 000 dollars (comparison only)
Working capital:	Not considered for comparison
Operating days/yr:	350
Location:	Scandinavia
Depreciation:	10% of fixed capital per annum
Period (yr):	10
Year used for costing purposes:	1979

SGW (for comparison only)

Cost items	Units used in costing	Factor/cost unit US dollars	Units required per ton product	Cost/ton of product
VARIABLE COSTS				
Raw materials (minus by-product credits)	m^3 solid ADT	\$ 39.5/m^3s. 474/ADT	2 0.19	79.00 90.06
Energy (minus energy credits)	kWh (MJ)	0.04/kWh	1600	64.00
Water	m^3	equal		
Labour				
(a) Operating	man-hr	equal		
(b) Maintenance	man-hr	equal		
overhead	% of labour cost	equal		
Miscellaneous				
TOTAL VAR. COST				233.06
FIXED COSTS		equal		
Plant overhead	% of labour costs	equal		
Local taxes and insurance	1% of fixed capital	180 000	1/170 000	1.06
Depreciation	10% of fixed capital	1 800 000	1/170 000	10.6
TOTAL PROD. COST				244.72
Return on investment	15% of total capital	2 700 000	1/170 000	15.88
Pollution control				2.09
GRAND TOTAL				262.69

6. Description of the PGW processing technology

6.1 Description of the unit operations used in the PGW production process

After barking, the feeding of the wood to the grinder is done batchwise into gas-tight grinding pockets. The actual grinding is done very similarly to the stone ground wood process. The mechanical pulp produced in this way has to be screened and may be somewhat bleached before it is used for newsprint stock preparation.

6.2 Specification of the materials and energy requirements for the process per ton of final end product (newsprint) PGW

The materials and energy requirements are examined by selecting a newsprint mill with a capacity of 500 tons paper per day (dryness 95 per cent) as a comparison base. The mill is assumed to buy power from an external grid, in addition to the amount that may be generated as back-pressure power in connection with the steam generation for the paper machine dryer. The steam and power departments are not dealt with in this report. The basic concept is described in the simplified flowsheet (Fig. 1).

The material and energy requirements for pressurized ground wood pulp for the production of 1 ton newsprint (95 per cent) are the following :

	PGW
- wood, m^3	2.22
- semi-bleached kraft air-dried kg	106
- power kWh	1930
- steam MJ	4200

Additionally, bleaching chemicals, peroxide and/or dithionite are used depending on the quality of the newsprint. This (as well as chemicals that may be used for waste treatment) is not taken into account, because it does not influence the comparison.

6.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the PGW production process

In the production of pressurized groundwood pulp, the pulping yield is assumed to be about 94 per cent. The yield loss appears mainly as waterborne waste which gives a BOD_7 load of approximately 18 kg BOD_7/ton newsprint produced.

6.4 Specification of the emission (effluent) solid waste standard applicable in Finland

At the time of this report, there are no emission effluents or solid waste discharge limits defined as certain numbers by law in Finland. The problems are dealt with on a case-by-case basis, individually for each mill. However, the National Water Board issues guidelines for waterborne wastes. These guidelines are given for discharge of suspended solids and oxygen-consuming matter (biochemical oxygen demand).

6.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

For comparison, an activated sludge waste-water treatment plant is assumed in order to reduce significantly the BOD_7-load on the recipient.

6.6 Specification of the airborne, waterborne and solid waste discharge into the environment

The BOD_7-load from the PGW-process which is about 8 kg BOD_7/ton newsprint is normally reduced in an effluent treatment plant.

Additionally, about 2.5 per cent of the wood entering the mill ends up as barking residue, which, however, is normally burned for steam and power production.

The PGW-process is not the source of any significant airborne waste.

The residual BOD_7-load to the recipient would be about 4 BOD_7/ton newsprint for PGW.

6.7 Cost-related data intended to permit comparison of the pressurized ground wood process with conventional thermo-mechanical pulp and stone ground wood processes for newsprint production

For a comparison of the above-mentioned processes, only departments where the differences in investment costs are to be found were considered when accounting for the fixed capital. This means that for pressurized ground wood pulping, the grinding and the waste-water departments were considered. The departments not included in the capital cost calculation are barking, paper machine (complete), steam and power generation and other supporting departments, as these investment costs remain approximately the same for both processes.

As there will be no significant difference in the working capital requirements, this is not considered here either.

These cost data in Table 3 are intended for comparison purposes only.

TABLE 3

Product : Newsprint
By-products: None
Plant capacity : 500 tons per day
Annual production: 170 000 tons
Process: Pressurized ground wood (PGW)
Fixed capital: 21 000 000 dollars (comparison only)
Working capital: Not considered for comparison
Operating days/yr.: 350
Location: Scandinavia
Depreciation: 10% of fixed capital per annum
Period (yr): 10
Year used for costing purpose: 1979

PGW (for comparison only)

Cost items	Units used in costing	Factor/cost unit US dollars	Units required per ton product	Cost/ton of product
VARIABLE COSTS				
Raw materials (minus by-product credits)	m^3 solid ADT	39.5/m^3s. 474/ADT	2.22 0.11	87.69 52.14
Energy (minus energy credits)	kWh (MJ)	0.04/kWh	1930	77.20
Water	m^3	equal		
Labour				
(a) Operating	man-hr	equal		
(b) Maintenance	man-hr	equal		
overhead	% of labour cost	equal		
Miscellaneous				
TOTAL VARIABLE COST				217.03
FIXED COSTS		equal		
Plant overhead	% of labour costs	equal		
Local taxes and insurance	1% of fixed capital	210 000	1/170 000	1.24
Depreciation	10% of fixed capital	2 100 000	1/170 000	12.35
TOTAL PRODUCTION COST				230.62
Return on investment	15% of total capital	3 150 000	1/170 000	18.53
Pollution control				3.02
GRAND TOTAL				252.17

7. Schematic comparison betwenn the TMP or SGW and the PGW technology

Areas for comparison	TMP	SGW	PGW
7.1 Materials and energy requirements per ton of newsprint produced			
Wood, m^3 solid	2.32	2.00	2.22
Pulp, air dry kg	74	190	106
Power, kWh	2430	1600	1930
7.2 Generation of wastes			
Airborne	negligible	negligible	negligible
Waterborne	28	8	18
Solid, bark	fired	fired	fired
7.3 Pollution control standards	non-existant	non-existant	non-existant
7.4 Discharge of waste			
Waterborne BOD_7/ton	6	2	4
7.5 Investment and production costs (for comparison only)			
Investment cost US dollars for 500 t/24 h	18	18	21
Production costs US dollars/ton	257	263	252

7.6 Other significant differences

As can be seen in Figure 2, electrical energy is an important part of mechanical pulping. With an increased energy price, the PGW-process is likely to be more competitive than TMP.

With the design of the first 14 commercial units for PGW, the equipment is likely to be developed in such a way that the initial investment cost may also be reduced.

8. Identification of needs for further research and development with regard to the pressurized ground wood technology

The pressurized ground wood process and the necessary equipment have been properly tested with the full-scale unit in Anjala (Finland). Continuous development work is, however, being carried out in order to improve the technology, e.g. in the following areas :

(a) Quality improvement in order to be able to reduce the need of semibleached kraft pulp to a minimum or finally to zero.

(b) Studying the possibilities to use other wood species than spruce for the process, e.g. tropical hardwoods.

(c) Reducing further the energy requirement for the process.

(d) Developing the heat recovery system for the process.

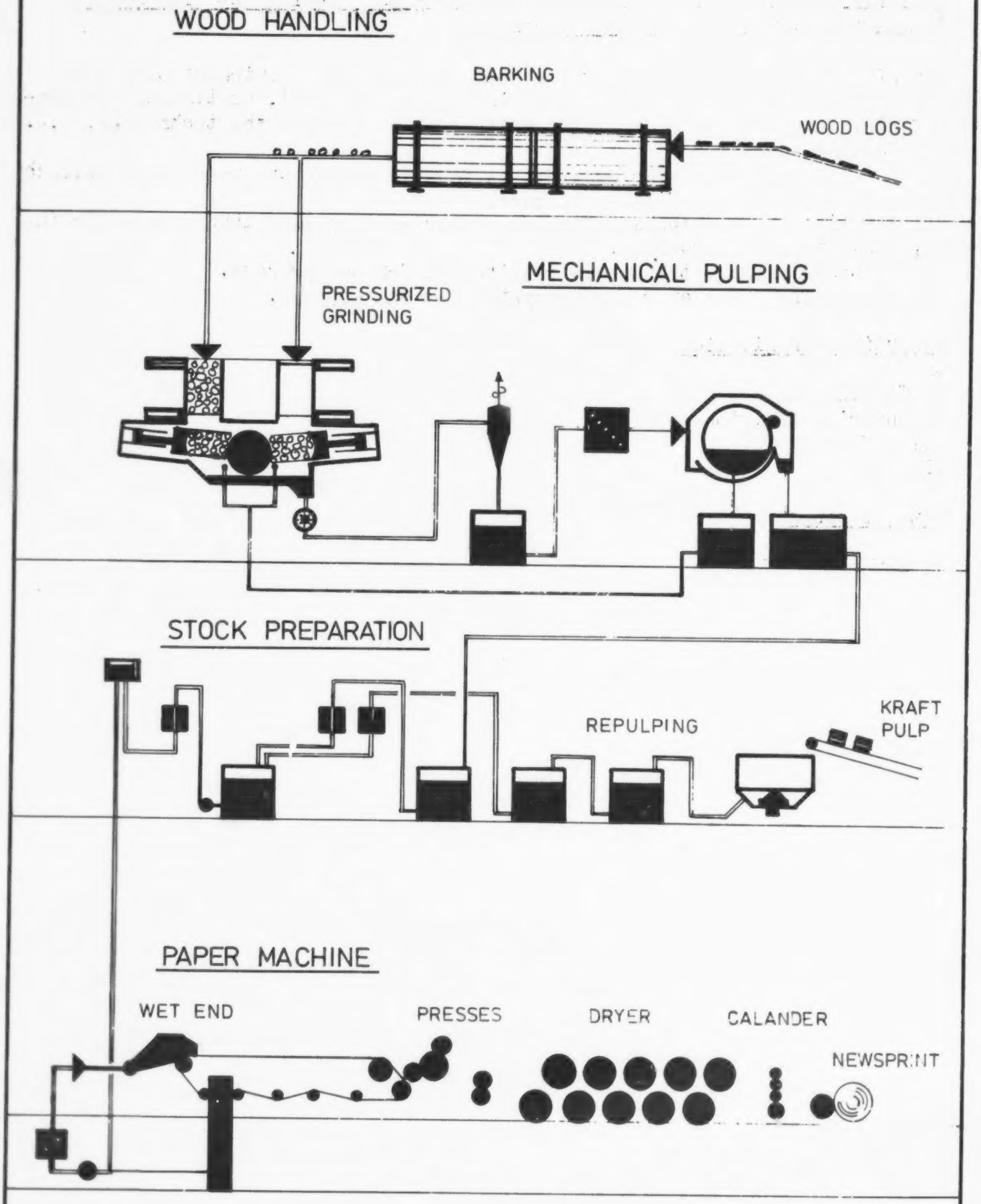
9. Reporting Organization

[illegible]
Oy TAMPELLA ab
Engineering Division
33100 TAMPERE 10
Finland

10. Date of report

23 November 1979

FIGURE 1


WOOD HANDLING
BARKING
WOOD LOGS
MECHANICAL PULPING
PRESSURIZED GRINDING
STOCK PREPARATION
REPULPING
KRAFT PULP
PAPER MACHINE
WET END
PRESSES
DRYER
CALANDER
NEWSPRINT

NEWSPRINT PRODUCTION FROM PRESSURIZED GROUNDWOOD.
PAPER PRODUCTION FLOWSHEET.

FIGURE 2

SPECIFIC POWER CONSUMPTION FOR NEWSPRINT PRODUCTION, CAPACITY 500 ton (95 %) / 24 h

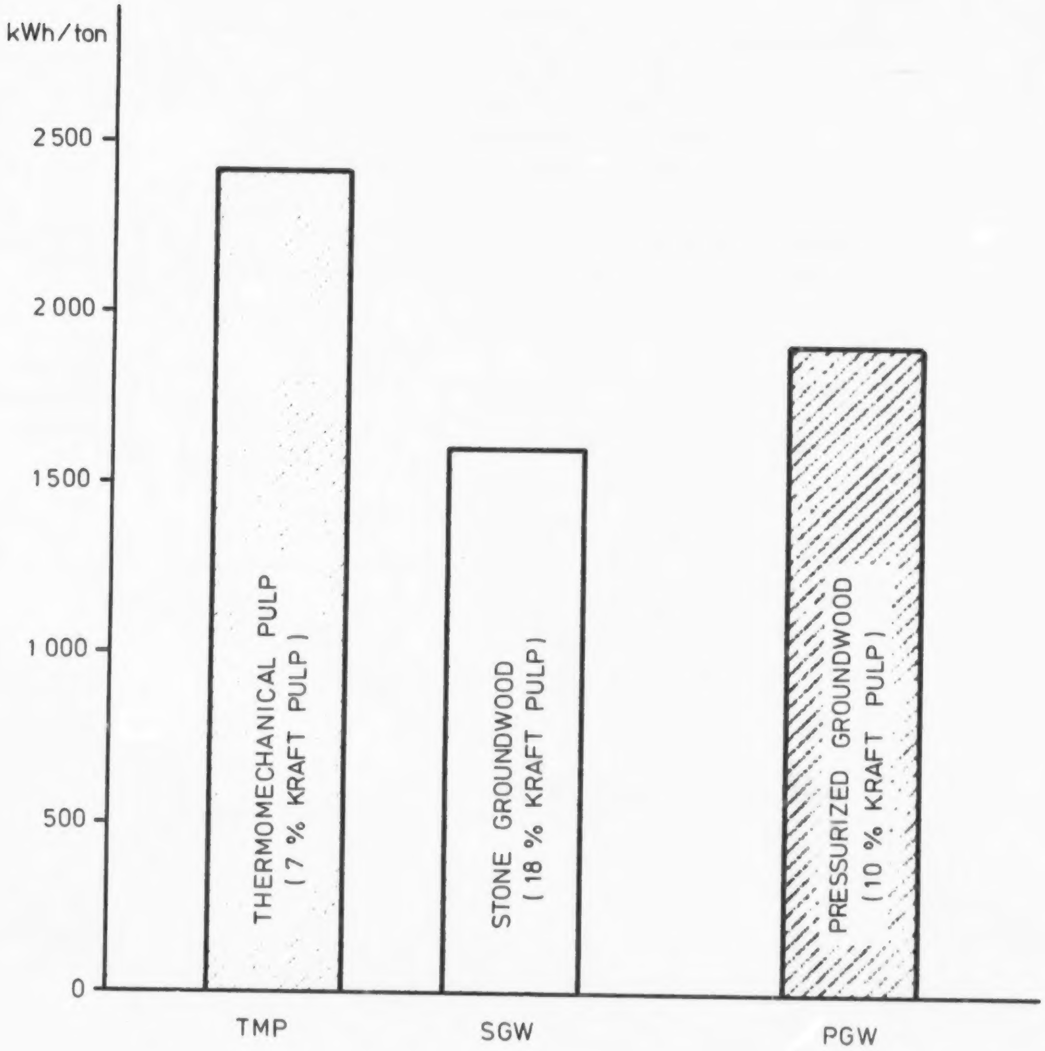
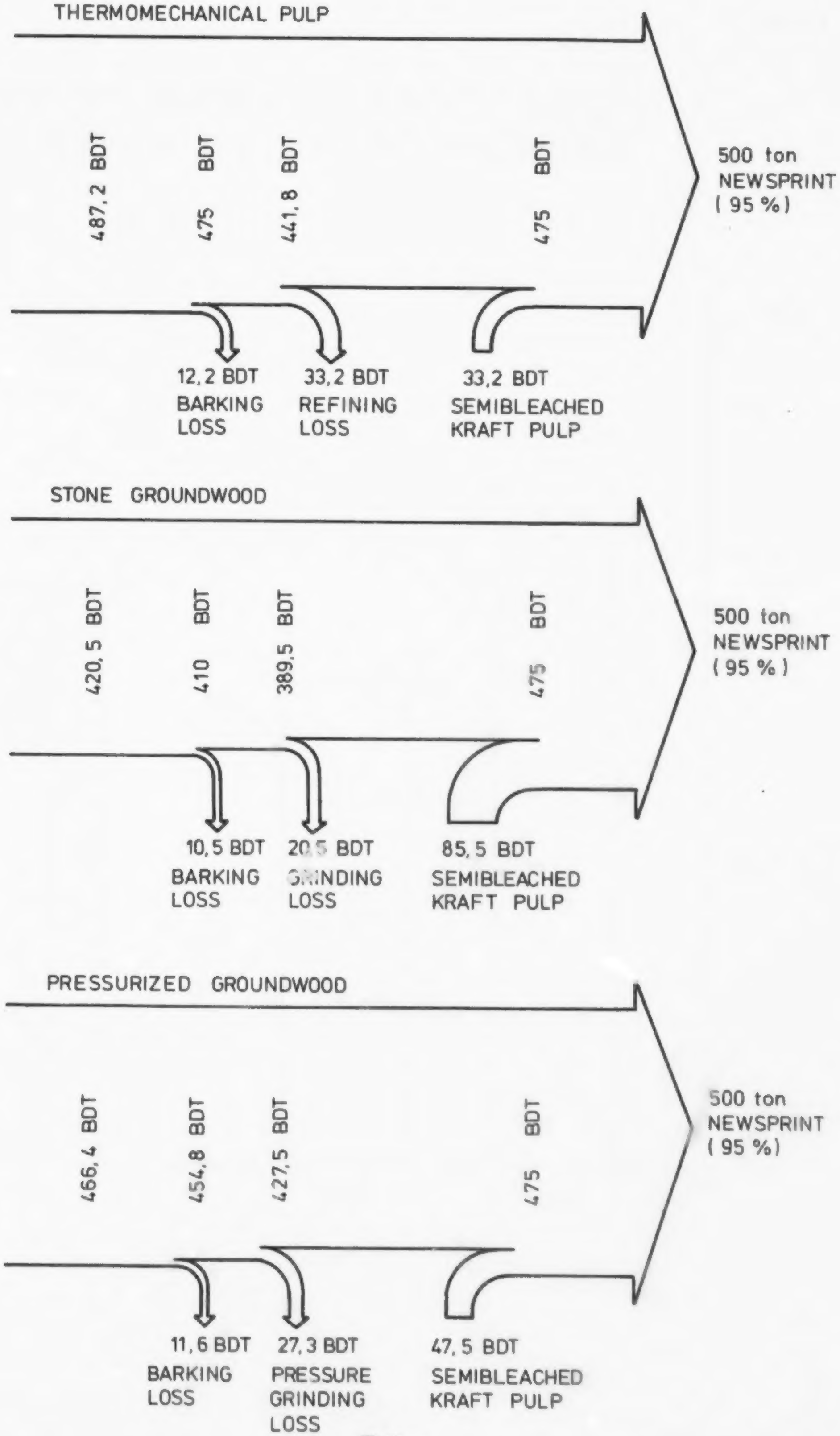


FIGURE 3 FIBER BALANCE


THERMOMECHANICAL PULP
487,2 BDT
475 BDT
441,8 BDT
475 BDT
500 ton NEWSPRINT (95 %)
12,2 BDT BARKING LOSS
33,2 BDT REFINING LOSS
33,2 BDT SEMIBLEACHED KRAFT PULP
STONE GROUNDWOOD
420,5 BDT
410 BDT
389,5 BDT
475 BDT
500 ton NEWSPRINT (95 %)
10,5 BDT BARKING LOSS
20,5 BDT GRINDING LOSS
85,5 BDT SEMIBLEACHED KRAFT PULP
PRESSURIZED GROUNDWOOD
466,4 BDT
454,8 BDT
427,5 BDT
475 BDT
500 ton NEWSPRINT (95 %)
11,6 BDT BARKING LOSS
27,3 BDT PRESSURE GRINDING LOSS
47,5 BDT SEMIBLEACHED KRAFT PULP

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

RESTRICTED
ENV/WP.2/5/Add.7
28 June 1981

ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

LOW TEMPERATURE WASTE HEAT DESALINATION (NORD-AQUA)

Transmitted by the Government of Finland

1. Identification of industry

Desalination of sea water (fresh water from the sea; drinking water production):
ISIC code : 4200 [1]

2. Basic characteristics of desalination process

Most of the sea water desalination capacity in the world is based on distillation processes (over 90 per cent). Membrane processes, reverse osmosis and electrodialysis are mainly used fof brackish water desalination. The basic principle of the distillation process is simply that of evaporating sea water and obtaining pure water by condensation. To decrease the energy consumption, the process is performed in several stages or effects and the heat of condensation is used to preheat a feed stream. To prevent scaling of heat transfer surfaces and corrosion of the plant, the sea water feed is normally deaerated and chemically treated.

3. Name of conventional desalination technology is Multistage Flash Distillation (MSF)

4. Description of MSF-Desalination technology

4.1 Description of the unit operations used inthe MSF-process

The essential features and major components of a MSF-plant are illustrated schematically in Figures 1 and 2. Figure 1 shows a conventional MSF-plant with acid treatment of feed water and brine recirculation. Figure 2 shows a once-through MSF-process, which becomes feasible after the introduction of high temperature additives. The process can be divided into the four following streams :

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex).

(a) Sea water stream

In the recirculation type of multi-stage flash process in Figure 1, cold sea water is pumped to the inlet of the heat rejection stages. The sea water is heated as it flows through the condenser tubes in these stages. After the sea water leaves the heat rejection section, a portion is returned to the sea. The remainder is chemically treated and flows to the decarbonator and the deaerator. In the decarbonator, the bicarbonate is converted to gaseous carbon dioxide and the greater part of this is vented; the deaerator removes oxygen and the remainder of the carbon dioxide from the makeup water. In once-through multi-stage flash process, the high temperature additive is dosed directly into the sea water stream, which flows to the condenser of the last stage.

(b) Brine recycle stream

Upon leaving the deaerator shown in Figure 1, the sea water mixes with the concentrated brine leaving the last stage of the rejection section. Before mixing, however, a portion of the concentrated brine from the last stage is removed to waste to maintain the proper brine concentration. The mixture of concentrated brine and freshly treated makeup solution is then pumped to the last (coolest) stage of the heat recovery section of the evaporator. As recycle brine, it flows through the tubes of the entire heat recovery section, receiving heat from the condensing product water and the reflashing distillate. The recycle brine leaves the heat recovery section and enters the brine heater where it is further heated to its top temperature. This additional heating is required to establish a flashing thermal potential. The top temperature of the brine is limited to avoid scale forming on the heater tubes. It depends on the type of feed water pretreatment used and the concentration range selected for the plant.

The brine leaves the brine heater and passes through a flow control valve. This valve maintains the brine pressure in the brine heater. The hot brine then is piped to the flashing chamber of the first (hottest) stage of the evaporator. A portion of the brine flashes to vapour. The vapour passes through entrainment separators (steam separators) and condenses while transferring its latent heat of vaporization to the recycle brine flowing in the tubes of the heat recovery stage. The condensate (product) is collected in trays. The amount of vapour evaporated and the brine saturation pressure at that stage are determined by the condensation rates.

As the brine flashes, it cools and then passes through flow control devices such as orifices or flow weirs, into the next, lower-pressure stage. The flashing process continues at progressively lower pressures until the brine leaves the last stage, after which a portion is removed as blowdown, and the balance is returned to the suction side of the recycle pump.

In the once-through multi-stage flash process shown in Figure 2, the brine flows on the tube side through a condenser in each stage. The brine leaves the condenser in the first (hottest) stage and enters the brine heater where it is further heated to its top temperature. The top temperature depends on the type and concentration of the high temperature additive used. After leaving the brine heater, the brine passes through a flow control to the flashing chamber of the first (hottest) stage of the evaporator. Inert gases present in sea water and the carbon dioxide formed in the heating section are vented from the two or three first stages. The evaporation process is similar to that of the recycle type of multi-stage flash process. From the last stage the concentrated brine is blown down on level control.

(c) Product water stream

The distillate produced from the condensing vapour flows along in trays, gradually increasing in volume until it leaves the last stage. It is then directed to the product water pump which pumps the product stream to the desired location. As the product flows from stage to stage, its temperature is reduced by flashing to a lower pressure in a manner similar to the brine stream. In some MSF-plants, the product water is sent to a product water cooler where its temperature is reduced to a range of 25° to 30 °C.

(d) Vapour streams

There are two major vapour streams. They are the stream admitted to the brine heater and the vapour resulting from liquid flashing in each stage. Condensate from the brine heater usually is returned to the boiler, while condensate originating from flashing becomes the product water. A minor vapour stream, with respect to size only, vents the noncondensable gases which must be removed from various stages to maintain design production rates, temperatures and pressures. Noncondensable gases are essentially air and carbon dioxide liberated during the evaporation process. If not removed, they impede the transfer of heat and reduce the desalting plant's capacity.

4.2 Specification of materials and energy requirements per ton of output

Materials and energy requirements per ton of output can only be specified by selecting a certain plant design and calculating the required figures.

Plant design basis :
- capacity: 1 000 m^3/d distillate
- process: once-through multi-stage flash
- sea water temperature : 25 °C
- brine top temperature : 115 °C
- brine temperature before brine heater : 107 °C
- water treatment : high temperature additive
- number of stages: 18
- heat source : extraction steam from power plant turbine
- type of vacuum equipment: water jet ejectors

Specific mass and energy consumptions per ton of product water :

Thermal energy for heating	298 MJ/t
- in the form of extraction steam	0,135 kg/t
corresponding fuel oil consumption = indirect energy consumption	8,06 kg/t
Electric energy consumption	5,04 kW/t
Scale prevention chemicals consumption	0,013 kg/t
Sea water feed	11,25 t/t

4.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

(a) Airborne wastes

When the thermal energy required in the process is generated from oil, the amount of sulphur dioxide depends on the sulphur content of the oil. Assuming a fuel oil containing 2 per cent sulphur, the amount of sulphur dioxide generated in the boiler is 0,35 kg SO_2/t product water.

(b) Waterborne wastes

Waterborne wastes are small in quantity and relatively harmless. The sources for waterborne wastes are feed water treatment and periodic acid cleaning of the plant. The net effect of acid treatment of feed water is that carbonates in sea water are changed to sulphates or chlorides, both of which are natural components of sea water. Polyphosphates and high temperature additives flow through the plant chemically unchanged. They do not cause any harm to sea life at the concentration normally applied. The periodic cleaning of heat-transfer surfaces by acid circulation causes a sour brine discharge at pH 4 or 5. Cleaning is, however, necessary only 2 or 6 times a year and the duration of sour brine discharge is only a few hours. If required the sour brine may be neutralized by caustic.

(c) Solid wastes

There are no wastes in solid form from a multi-stage flash desalination plant.

4.4 Specification of the emission and effluent standards in Finland

There are no official standards for the emission of sulphur dioxide into the atmosphere. Chloride or sulphate concentration of effluents into sea is not limited in Finland.

4.5 Specification of pollution control measures necessary for compliance with existing standards

No add-on pollution control measures are required for a multi-stage flash desalination plant to comply with existing standards.

4.6 Specification of airborne, waterborne and solid discharges into the environment

Discharges into the environment are those generated in the process as specified in 4.3.

4.7 Cost-related data intended to permit comparison of low temperature waste-heat desalination process with conventional multi-stage flash evaporation

Product : Fresh water
By-products: None
Plant capacity: 1 000 t/d
Annual production: 350 000 t/a
Process: once-through multi-stage flash, operating on extraction steam
Fixed capital: US$ 2 065 000
Working capital: US$ 153 000
Operating days/year: 350
Location: Finland
Depreciation: 10% of fixed capital per annum
Period: 10 years
Year used for costing purposes: 1979

CONVENTIONAL MULTI-STAGE FLASH EVAPORATOR

COST ITEM	Units used in costing	Price/cost unit in US dollars	Units required per ton product	Cost/ton of product
VARIABLE COSTS				
Raw materials				
Belgrad Ev-antiscale	kg	4.63	0.013	0.060
Sea water	ton	0.0	11.25	-
Energy				
Thermal energy (extract. steam)	ton	10.5	0.135	1.417
Electric energy	kWh	0.06	5.04	0.302
Labour				
Operating	man hour	10	0.016	0.160
Maintenance over-head	man hour	12	0.020	0.240
Miscellaneous				0.080
TOTAL VARIABLE COSTS				2.259
FIXED COSTS				
Plant overhead	100% of labour cost	10	0.016	0.160
Local taxes and insuracce	1% of fixed cap.	20 650	1/350 000	0.059
Depreciation	10% of fixed capital	206 500	1/350 000	0.590
TOTAL PROD. COST				3.068
Return of investment	25% of total capital	554 500	1/350 000	1.584
Pollution control				-
GRAND TOTAL				4.652

5. Name and state of developeent of low- and non-waste processing technology

The process is called Nord-Aqua Waste Heat Desalination; a convenient abbreviation used for it is WHD. The WHD-process is at the advanced pilot plant stage. Three pilot plants have been built. The last one was a full scale pilot plant with a capacity of 500 tons distillate per day. It was built in 1978 by Navire Oy in Naantali (Finland). The plant was mounted on a barge for better mobility and to facilitate future tests with natural thermoclines. Tests made with the pilot plant in Naantali (Finland) proved the design to meet the requirements for capacity and distillate quality without exceeding the energy consumption calculated.

6. Description of Nord-Aqua waste heat desalination technology

6.1 Description of the unit processes used in the WHD-process

The basic idea of the WHD-process is to utilize the thermal energy available in two sea-water streams having different temperatures to distill the water. Essential in the WHD-process is its ability to utilize small temperature differences (5 to 15 °C) at a low temperature level (10 to 40 °C). The distillation process itself is similar to that in the MSF-process. Figure 3 gives a schematic diagram of the WHD-process.

The process can be divided into the two following streams :

(a) Warm sea water stream

The warm sea-water stream can be the cooling water return of a coastal power station or industrial plant or warm surface water. It is first pumped to a deaerator, where the dissolved gases are removed. The deaerator is a special type of packed column. The non-condensable gases are pumped out by water jet ejector. The pressure in the deaerator is slightly above the vapour pressure of the warm sea water. Good deaeration is essential for the performance of the condensers. From the deaerator the warm sea-water stream is fed to the flashing chamber of the first (hottest) stage of the evaporator. A fraction of the warm sea-water stream is flashed into the vapour. The vapour flows through the entrainment separator to the condenser. The warm sea water is taken through the flow weirs to the flashing chamber of the next stage and the flashing process continues. Due to the small temperature difference, the optimum number of stages is normally three. From the last stage the warm sea water (brine) is fed through the water jet ejector and vacuum leg back to sea. The brine flow is thus utilized to pump out the non-condensables from the two first stages.

(b) Cold sea water stream

A cold sea-water stream is used as cooling water in the WHD-process. In a land-based plant, the cold sea water stream is similar to the cooling water supply of the plant which produces the waste heat used in desalination. In a barge-mounted plant, utilizing natural thermocline,the cooling water stream has to be taken deep enough to ensure an adequate temperature difference. The cooling water is pumped into the tubes of the condenser of the last stage. A side stream is taken to the water jet ejector, which pumps out the non-condensables from the last evaporator stage. The cooling water flows through the condenser tubing in all stages, takingup the heat of condensation from the condensing vapour. From the condenser, the cooling water flows through the water jet ejector and vacuum leg back to the sea. Condensate is collected in trays in each stage and is pumped by the product pump to the desired location. The capacity of a given WHD-process is directly proportional to the temperature difference between the warm sea-water feed and the cooling water. The functional minimum temperature difference is about 3 °C due to the boiling point elevation and various losses in the actual process. The minimum temperature difference for economical operation at today's energy prices lies at 7 °C.

6.2 Specification of materials and energy requirements of the Nord-Aqua WHD-process per ton of fresh-water output

The main streams for a 1 000 m^3/d WHD-plant are specified in Figure 3. The design is based on the following data :

- capacity	1 000 tons distillate/day
- warm sea water inlet temperature	25 °C
- cold sea water inlet temperature	15 °C
- warm sea water outlet temperature	20.7 °C
- source for warm sea water	cooling water return from a coastal power station

(a) Specific flow rates and energy consumption per ton of fresh water production:

Warm sea-water feed	134 t/t of distillate
Cooling water flow	134 t/t of distillate
Electric energy consumption	6.86 kWh/t of distillate

Large sea water flows

The temperature drop of the warm sea water in the evaporator is only 4.3 °C. The corresponding amount of sensible heat can evaporate less than 1 per cent of the warm sea-water feed. Thus, the warm sea-water feed is more than 100 times larger than the fresh-water production. To get the same temperature difference between condensing vapour and cooling water in each stage, the cooling water flow-rate has to be equal to the warm sea-water feed.

The pumping cost caused by large sea water streams is minimized by utilizing a vacuu leg. The pumps thus have only to overcome the frictional pressure drop in the plant.

Deaeration and vacuum pumps

Due to the large flow rate and low temperature level of the warm sea water feed the volume of non-condensable gases to be removed from the deaerator is very large, too. The only economical way of compressing the non-condensable gases to atmospheric pressure is by water jet ejector utilizing the cooling water return from the evaporator. The water jet ejector has to perform very close to the absolute limit of the vapour pressure of the cooling water return. Because any of the ejector manufacturers did not quote for such duty the only way was to design and experiment until the required duty was met. The development work resulted with an ejector, which deviates considerably from the normal water jet ejectors.

Condenser for very low pressure drop

The condenser in a WHD-process operates at conditions somewhat similar to the condensers for thermal power stations. In a WHD-condenser, however, the temperature difference available is less while the amount of non-condensable gases is greater.

These facts make designing the condenser for WHD-process a very demanding task. To prevent inert gas from blanketing in the condenser, a high velocity should be used. High vapour velocity is, however, accompanied by a high pressure drop, which lowers the condensation temperature and thus gives poor performance. In an ideal condenser for the WHD-process, the vapour velocity has to be as low as possible but high enough to prevent inert gas from blanketing.

6.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the Nord-Aqua WHD-process

(a) Airborne wastes

There are no airborne wastes generated in the WHD-process. The only flow vented to the atmosphere is the non-condensable gases removed from the warm sea-water feed. These non-condensable gases are essentially air dissolved into the sea water.

(b) Waterborne wastes

The WHD-process removes less than 1 per cent of the warm sea-water feed as distilled water and returns the rest to the sea. The WHD-process thus does not generate any waterborne wastes. As a matter of fact, the WHD-process decreases the effect of thermal pollution caused by coastal power stations and industrial plants. The WHD-process substitutes a cooling water return having a temperature of 10 °C above ambient sea water with two equal streams having a temperature of 5 °C above ambient sea water.

(c) Solid wastes

No solid wastes are generated in the WHD-process.

6.4 Specification of the emission/effluent/solid waste standards applicable in Finland

There are no such standards in Finland which could be applied to the WHD-process.

6.5 Specification of pollution control measures

No pollution control measures are required.

6.6 Specification of the airborne, waterborne and solid waste discharges to the environment

The waste discharges to the environment are those specified in point 4.3.

6.7 Cost-related data to permit comparison of low- and non-waste technology with conventional technology

Product: Fresh water
By-products: None
Plant capacity: 1 000 t/d
Annual production: 350 000 t/a
Process: Low temperature waste heat desalination
Fixed capital: US$ 1, 842,000
Working capital: US$ 160,000
Operating days/year: 350
Location: Finland
Depreciation: 10% of investment per year
Year used for costing purposes: 1979

NORD-AQUA WASTE HEAT DESALINATION

COST ITEMS	Units used in costing	Price/cost unit in US $	Units required per ton product	Cost/ton product/US$
VARIABLE COSTS				
Raw materials				
Warm sea water	ton	0,0	134	0,0
Cold sea water	ton	0,0	134	0,0
Energy				
Thermal energy	MJ		0,0	0,0
Electric energy	kWh	0,06	6,86	0,412
Labour				
Operating	man hour	10	0,016	0,160
Maintenance overhead	man hour	12	0,008	0,096
Miscellaneous				0,080
TOTAL VARIABLE COST				0,764
FIXED COSTS				
Plant overhead	100% of labour cost			0,160
Local taxes and insurance	1% of fixed capital	18 420	1/350 000	0,053
Depreciation	10% of fixed capital	184 200	1/350 000	0,526
TOTAL PROD. COST				1,503
Return on investment	25% of total capital	500 500	1/350 000	1,430
Pollution control				-
GRAND TOTAL				2,933

7. Schematic comparison between the conventional and the low- and non-waste technology

Areas for comparison	Multistage flash distillation a	Low temp. waste heat desalination b	Difference b - a
7.1 Materials and energy requirements			
Warm sea water required t/t of product	nil	134	± 134
Cold sea water required t/t of product	11,2	134	± 122,8
Belgrad EV-antiscale kg/t of product	0,013	nil	∓ 0,013
Thermal energy MJ/t of product	298	nil	∓ 298
Electric energy	5,04	6,86	± 1,82
7.2 Generation of wastes	negligible	negligible	
7.3 Pollution control measures	not required	not required	
7.4 Waste discharges	negligible	negligible	
7.5 Investment and production costs			
Investment cost $ for 1000 t/d plant	2 065 000	1 842 000	- 223 000
Production cost $/ton for 1000 t/d plant	3 068	1 503	- 1 565
7.6 Other significant differences			
Risk of corrosion	big	small	
Risk of scaling of heat transfer surfaces	big	small	

7.7 Other significant differences between the conventional multi-stage flash and waste-heat desalination process

(a) Materials of construction and corrosion

The multi-stage flash processes normally operate with top brine temperature varying from 90 °C to 115 °C. The materials normally used in multi-stage flash plants are carbon steel or epoxy coated carbon steel for the shell in the low temperature end and copper, nickel and stainless steel or carbon steel for the evaporator shell in the high temperature end, with aluminium, brass or copper-nickel for the condenser tubing.

The rate of corrosion of construction materials accelerates with increasing temperatures, the rate of corrosion is very sensitive to the oxygen content and pH of the brine. With low-temperature waste-heat desalination, the corrosion problems are smaller due to the low operating temperature and cheaper construction materials may be used in the WHD-plants. In addition, higher on-stream factors are likely to be reached.

(b) Scale formation and prevention

Scale formation on the heat transfer surfaces in contact with brine begins at the temperature of 50 to 60 °C. Therefore, all multi-stage flash plants apply some type of prevention method. There are three basic types of scale prevention methods :

- polyphosphate addition, maximum brine temperature : 90 °C
- acid treatment, maximum brine temperature : 120 °C
- high temperature additives, maximum brine temperature : 120 °C

The scale prevention method makes the multi-stage flash process more complicated. Failure in the scale prevention system causes rapid fouling of the heat transfer surfaces.

In the WHD-process, no scale-prevention methods are required due to the low temperature level.

8. Identification of needs for further research and development with regard to the Nord-Aqua waste heat desalination technology

The process itself and the most critical pieces of the equipment have been adequately tested in the full scale pilot plant. The areas requiring further study and development work are :

- The economic feasibility and the type of additional equipment required to utilize natural thermoclines in the oceans for the production of fresh water.

- The optimum construction of a low-temperature waste-heat desalination plant for very large capacities (over 10 000 m^3/d)

- The design of cooling water systems of new power stations and industrial plants for smaller flow rates and higher temperature differences to enable more efficient utilization of the waste heat by the WHD-process.

9. Reporting organization

Nord-Aqua Oy
Vuorimiehenpuistikko 4 D
00140 Helsinki 14
Finland

10. Date of report

10 October 1979

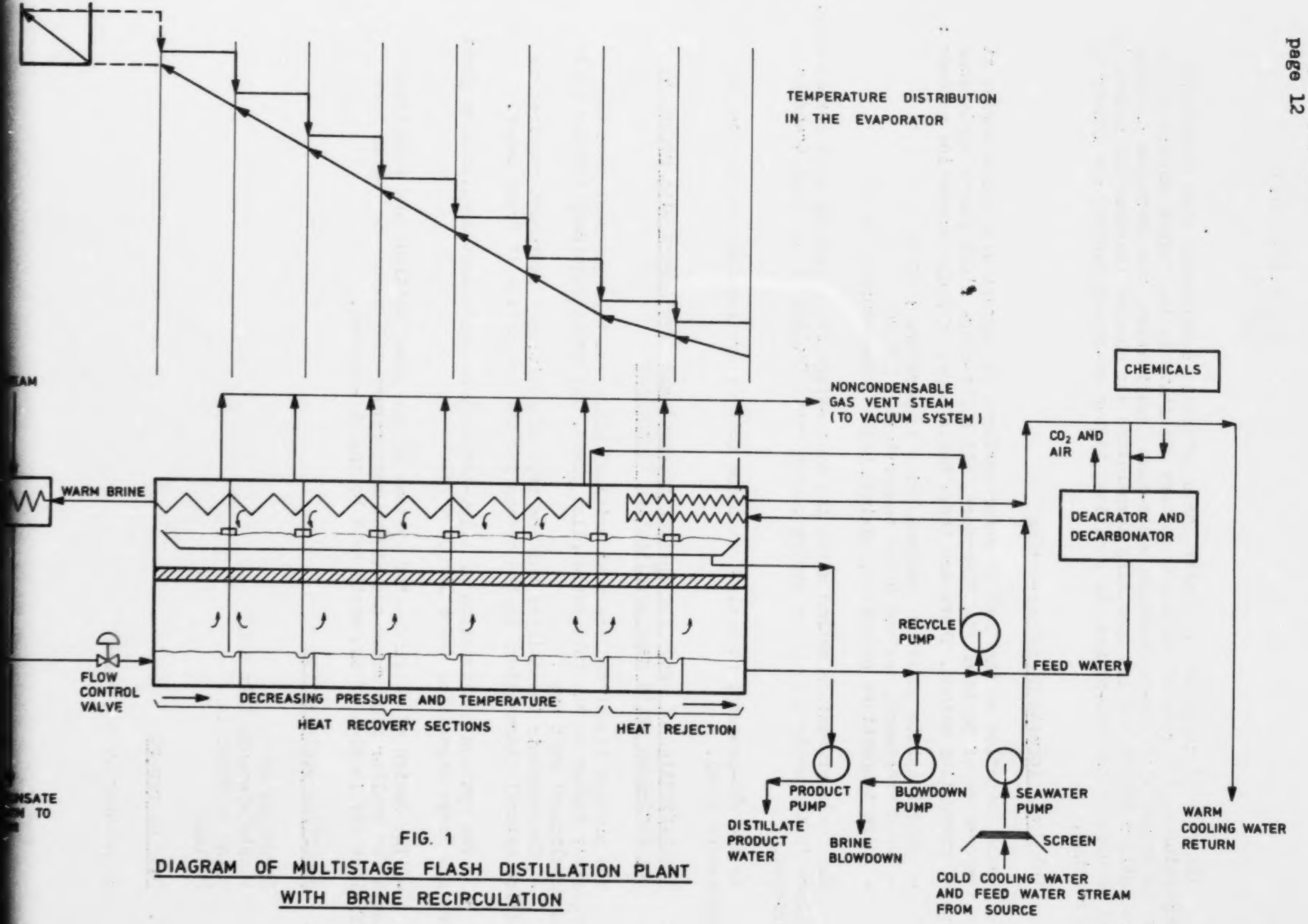

TEMPERATURE DISTRIBUTION
IN THE EVAPORATOR
EAM
NONCONDENSABLE
GAS VENT STEAM
(TO VACUUM SYSTEM)
CHEMICALS
CO_2 AND
AIR
WARM BRINE
DEACRATOR AND
DECARBONATOR
RECYCLE
PUMP
FEED WATER
FLOW
CONTROL
VALVE
DECREASING PRESSURE AND TEMPERATURE
HEAT RECOVERY SECTIONS
HEAT REJECTION
NSATE
N TO
PRODUCT
PUMP
BLOWDOWN
PUMP
SEAWATER
PUMP
WARM
COOLING WATER
RETURN
DISTILLATE
PRODUCT
WATER
BRINE
BLOWDOWN
SCREEN
COLD COOLING WATER
AND FEED WATER STREAM
FROM SOURCE

FIG. 1

DIAGRAM OF MULTISTAGE FLASH DISTILLATION PLANT
WITH BRINE RECIPCULATION

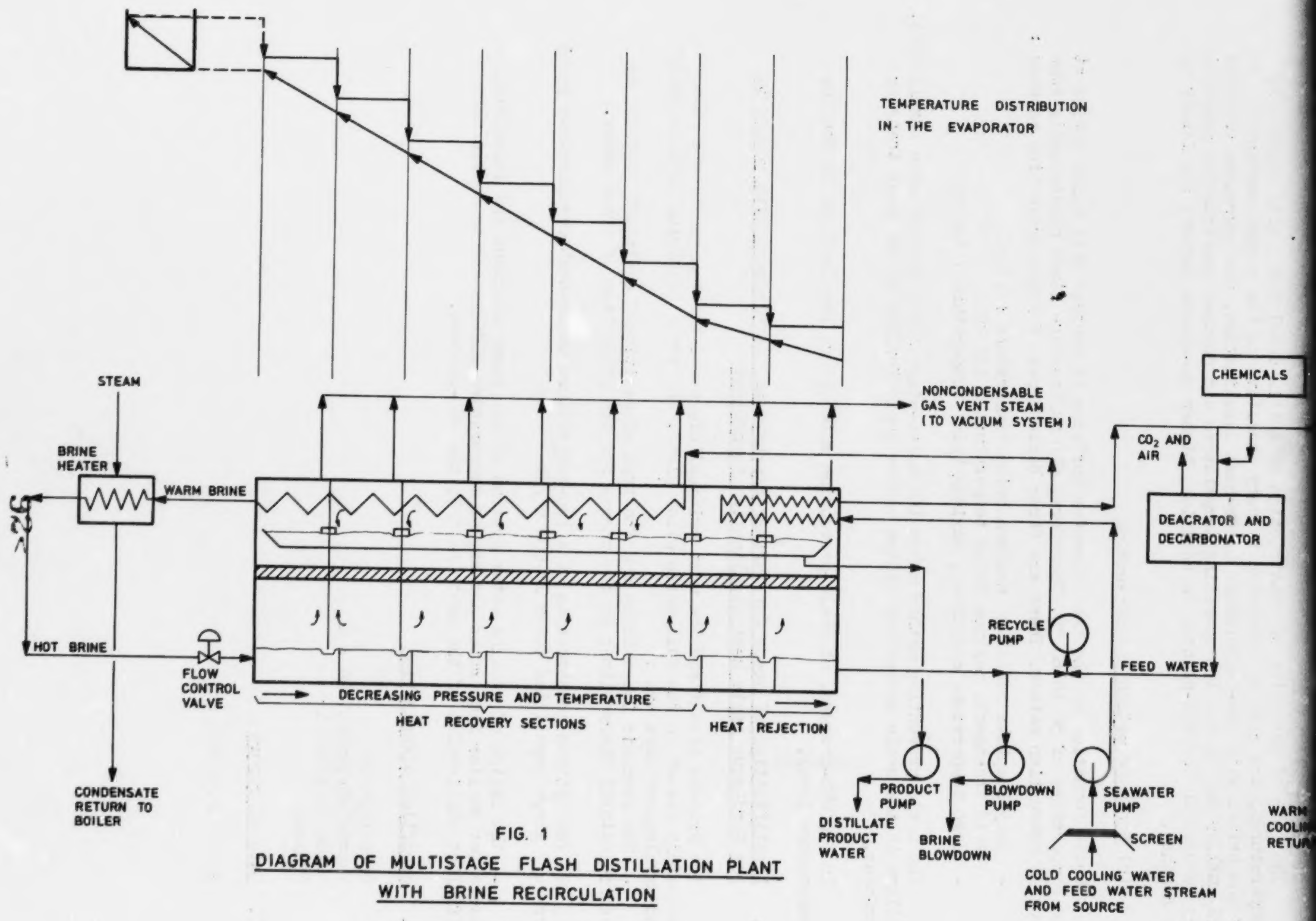

TEMPERATURE DISTRIBUTION IN THE EVAPORATOR
STEAM
BRINE HEATER
WARM BRINE
HOT BRINE
FLOW CONTROL VALVE
CONDENSATE RETURN TO BOILER
NONCONDENSABLE GAS VENT STEAM (TO VACUUM SYSTEM)
CHEMICALS
CO_2 AND AIR
DEACRATOR AND DECARBONATOR
RECYCLE PUMP
FEED WATER
DECREASING PRESSURE AND TEMPERATURE
HEAT RECOVERY SECTIONS
HEAT REJECTION
PRODUCT PUMP
DISTILLATE PRODUCT WATER
BLOWDOWN PUMP
BRINE BLOWDOWN
SEAWATER PUMP
SCREEN
COLD COOLING WATER AND FEED WATER STREAM FROM SOURCE
WARM COOLI RETUR

FIG. 1

DIAGRAM OF MULTISTAGE FLASH DISTILLATION PLANT WITH BRINE RECIRCULATION

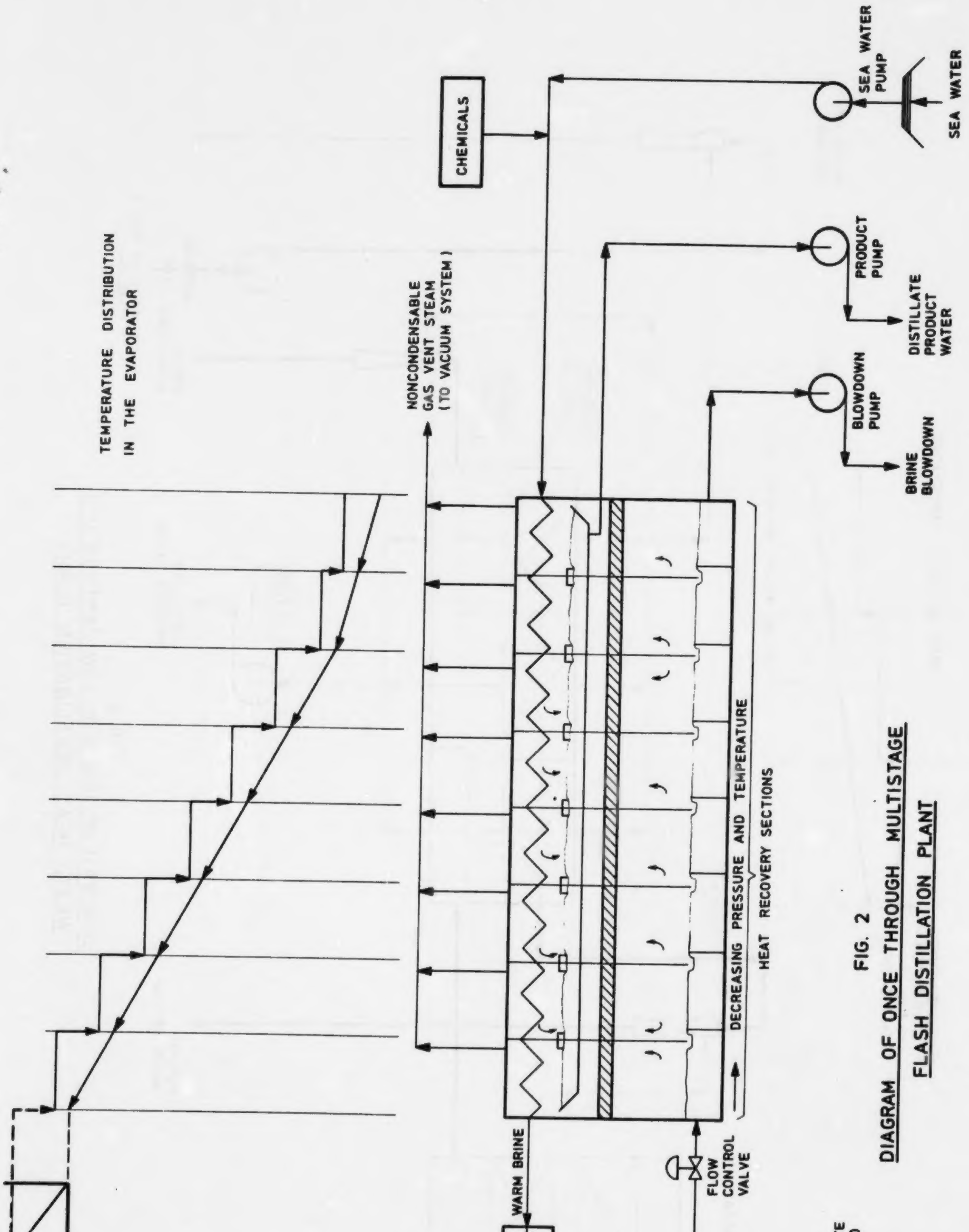

TEMPERATURE DISTRIBUTION
IN THE EVAPORATOR
NONCONDENSABLE
GAS VENT STEAM
(TO VACUUM SYSTEM)
CHEMICALS
SEA WATER
PUMP
SEA WATER
PRODUCT
PUMP
DISTILLATE
PRODUCT
WATER
BLOWDOWN
PUMP
BRINE
BLOWDOWN
DECREASING PRESSURE AND TEMPERATURE
HEAT RECOVERY SECTIONS
WARM BRINE
STEAM
BRINE
HEATER
FLOW
CONTROL
VALVE
HOT BRINE
CONDENSATE
RETURN TO
BOILER

FIG. 2

DIAGRAM OF ONCE THROUGH MULTISTAGE

FLASH DISTILLATION PLANT

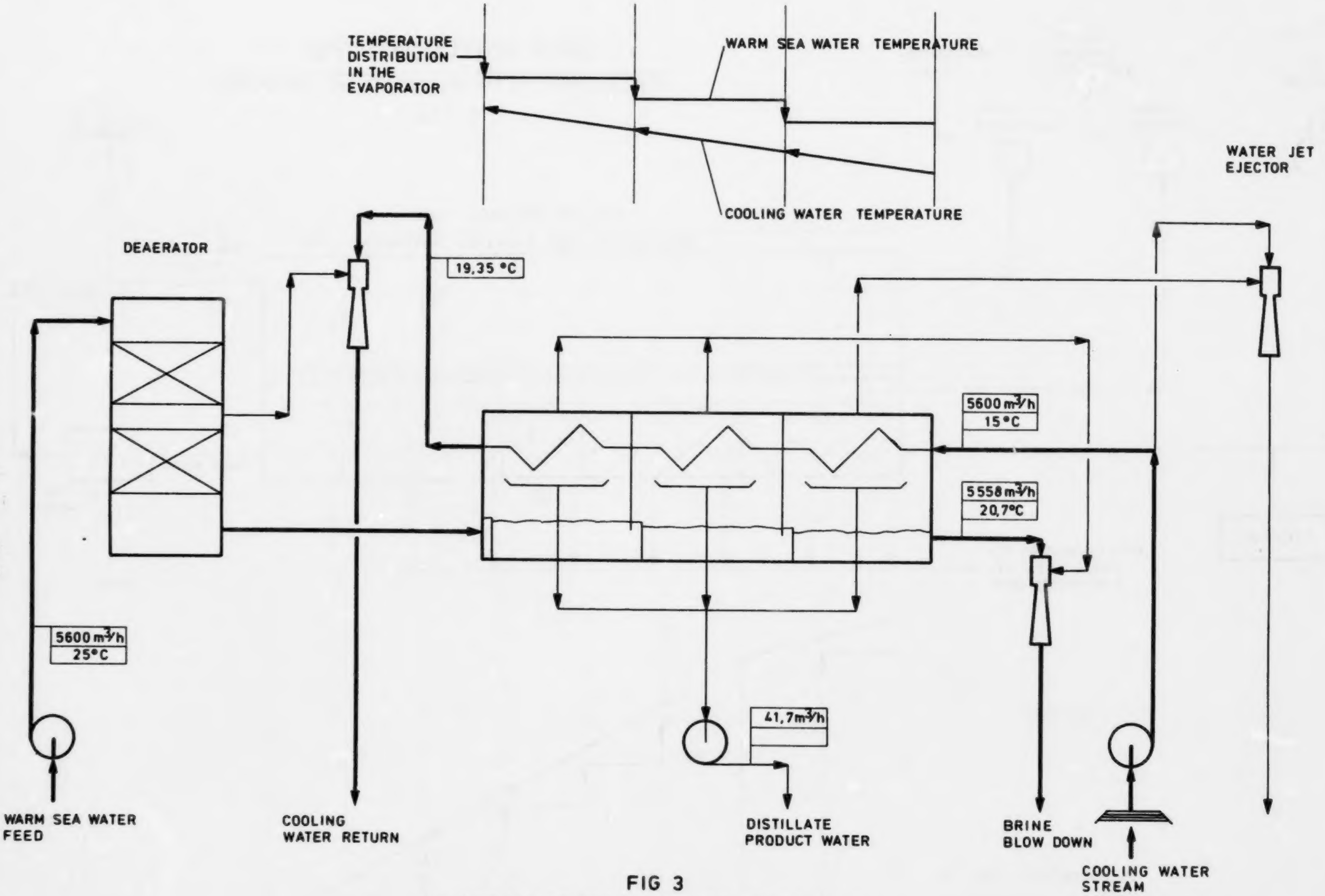

TEMPERATURE DISTRIBUTION IN THE EVAPORATOR
WARM SEA WATER TEMPERATURE
COOLING WATER TEMPERATURE
WATER JET EJECTOR
DEAERATOR
19,35 °C
5600 m^3/h
15 °C
5558 m^3/h
20,7 °C
5600 m^3/h
25 °C
41,7 m^3/h
WARM SEA WATER FEED
COOLING WATER RETURN
DISTILLATE PRODUCT WATER
BRINE BLOW DOWN
COOLING WATER STREAM

FIG 3

DIAGRAM OF 1000 m /d LOW TEMPERATURE WASTE HEAT DESALINATION PLANT

UNITED NATIONS

ECONOMIC AND SOCIAL COUNCIL

RESTRICTED

ENV/WP.2/5/Add.8
2 July 1981

ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste Technology and Re-utilization and Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

CONTINUOUS HARDENING AND ZINC-COATING (ZINQUENCH)

Transmitted by the Government of Finland

1. Identification of industry

Hot dip galvanizing. ISIC code [1]: 3710

2. Basic characteristics of production process

There are numerous approaches to prevent corrosion of steel but none so effective, practical and economic as metallic zinc coatings applied by the hot dip galvanizing process. Zinc is strongly resistant to the corrosive action of normal environments and therefore provides long-term protection. Hot dip galvanizing prevents corrosion of steel by providing :

(a) A tough, durable barrier coating of metallic zinc which completely seals the steel from corrosive environments.

(b) Cathodic or sacrificial protection. The zinc coating corrodes very slowly in a way preferential to the steel base, preventing corrosion of small areas of steel, which may be exposed through accidental damage to the coating or at cut edges or drilled holes. The hot dip galvanizing process produces a durable, abrasion-resistant coating of metallic zinc and zinc-iron alloy layers metallurgically bonded to the steel base and completely covering the item. The galvanized coating is subject to corrosion but at a predictably slow rate, between one tenth and one thirtieth of steel, the rate depending on the environment to which the coating is exposed.

Metallic zinc is anodic to steel. That is why, in the presence of an electrolyte, the anodic zinc coating on a galvanized article corrodes preferentially to the cathodic steel underlying metal, preventing corrosion of small areas which may be exposed

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.3/5/Annex).

through accidental damage to the coating. This cathodic or sacrificial protection continues as long as the zinc coating remains. In most environments, the rate of consumption of the zinc coating is low and protection is provided for very long periods.

Hot dip galvanizing is a process in which an adherent, protective coating of zinc and zinc compounds is developed on the surfaces of iron and steel products by immersing them in a bath of molten zinc at temperatures of 450 ° to 560 °C. The protective coating consists of several layers : those closest to the base metal are composed of iron-zinc compounds; the outer layer consists almost entirely of zinc. Differences in coating commosition, bath temperature, time of immersion, and rate of cooling can result in significant changes in the appearance and properties of the coating.

Galvanized coatings are produced on iron and steel primarily to provide protection against corrosion of the basis metal. Wherever steel is exposed to atmospheric, soil or water corrision, coating with zinc is a standard and effective method of protection.

In the manufacture of certain steel parts it is usually necessary to improve machinability while retaining mechanical properties of steel by heat treatment. Heat treatment is an operation or combination of operations involving the heating and cooling of a metal in the solid state for the purpose of obtaining certain desirable conditions or properties. Two types of heat treatment are principally used for steels :

(a) Conditioning treatments, i.e. annealing, that prepare the steel for certain fabricating operations.

(b) Quenching and tempering, i.e. hardening, to improve mechanical properties of the steel.

3. Name of conventional processing technology

Conventional heat treatment process and hot dip galvanizing.

4. Description of conventional processing technology

The conventional process of galvanizing is usually carried out in two stages :

(a) The first stage is quenching and tempering to improve mechanical properties of the steel.

(b) The second stage is the hot dipping to produce an adherent, protective coating of zinc on the surface of steel.

4.1 Description of unit operations

The conventional procedure (Fig. 1) of hot dip galvanizing, for example in the manufacture of high strength, class 8.8 bolts, includes two different stages : quenching and tempering of the bolts to be galvanized and zinc coating with necessary pretreatments. Temperatures in these stages are usually about 900 °C in austenitizing, i.e. hardening annealing, and about 500 °C in tempering. The temperature of the galvanizing bath is about 450 to 560 °C. In the conventional process, bolts are quenched in oil after austenizing to a temperature of about 60 °C. The next stage is tempering, in which the bolts are heated again to the temperature of about 500 °C. During tempering, iron and alloying elements oxydize and form a layer on the surface of the bolt and makes it very difficult for the zinc to adhere to the bolt. That is why different pretreatments are involved before hot dipping to remove surface oxide. These steps may also involve storing and transport operations if hardening and galvanizing are performed in different places.

The metal to be coated with zinc is at first thoroughly cleaned by various possible methods. It has to receive a coating of flux which enables the molten zinc to adhere to the base metal when it is immersed in the zinc pot. In the so-called wet process, the flux layer floats on the surface of the zinc bath, and work pieces are immersed through the flux in a bath. After a sufficient time for bolts to wet and alloy with the zinc, these are withdrawn from the bath. The excess zinc is drained from the bolts immediately by spinning in a basket.

4.2 Specification of materials and energy requirements per ton of output

For comparison see 7.

4.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

In the conventional process of hot dip galvanizing, the use of flux generates airborne, waterborne and also some solid wastes in the production process. The flux usually is made by mixing ammonium chloride and zinc oxide to form the monoamine of zinc chloride. In the ensuing reaction, the flux takes the form of a foam. Preparation of this flux can be unpleasant due to the evolution of irritating fumes. An average analysis of such flux fumes is as follows :

Zn	5 - 20 per cent
Cl	30 - 50 per cent
NH_4	15 - 40 per cent
Al	maximum 10 per cent
Fe	minimum 1 per cent

After hot-dipping, flux residues must be removed by water rinsing which generates waterborne wastes.

4.4 Specification of the emission/effluent/solid waste standards applicable in Finland

There are no official standards concerning the emission of effluent or solid waste for hot dip galvanizing plants in Finland.

4.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

No add-on pollution control measures are required for compliance with existing standards.

4.6 Specification of airborne, waterborne and solid waste discharges into the environment

Discharges are those specified in 4.3.

4.7 Cost-related data intended to permit comparison of low-and non-waste technology with conventional technology

For comparison see 7.

5. Name of low- and non-waste processing technology

Zinquench process

6. Description of low- and non-waste processing technology

In the Zinquench process (Fig. 2), work pieces are first austenitized at a normal hardening temperature of 900 °C; they are then quenched in the zinc bath where the hot dip coating also occurs. After a sufficient time, work pieces are taken from the bath to a centrifuge, which removes the excess zinc. The final stage is water cooling.

6.1 Description of the unit processes used in the production process

The temperature of an aluminium alloyed galvanizing bath used in the Zinquench process is about the same as the temperature of the bainite transformation of steel used in the manufacture of high strength bolts, i.e. to 410 °C. This allows the hardening and zinc coating processes to be combined. Some stages of the conventional process are unnecessary and are omitted (Fig. 3). The bainitic structure generated in steel in the Zinquench process and tempered martensite, the structure of steel after quenching and tempering, have similar properties. In the Zinquench process, a bainite hardening occurs in the galvanizing bath.

In the conventional procedure (Fig. 1), during galvanizing small bolts and especially threads will temper further and become softer. In the Zinquench process there is no excess tempering; on the contrary the threads are harder than the core (Fig. 4). The structure of the Zinquench coating is similar to that obtained in conventional galvanizing. The process needs no flux treatment before hot dipping because the bolts are in the austenitizing furnace in an inert atmosphere and the steel surface thus remains unoxidized. In the Zinquench process there is a decreasing and activating operation before the austenitizing furnace.

An excess in the energy requirements is reached because the hot work pieces from the furnace retain sufficient heat and the galvanizing bath does not need any further heating (Figs 1 and 2). Because in the Zinquench process no flux is used, there is no danger of so-called flux corrosion. That is why there are no waterborne wastes generated in the Zinquench production process.

6.2 Specification of materials

(1) Steel base

Zinquench process is first adapted in the manufacture of high strength (class 8.8) bolts. In the manufacture of high strength bolts the following properties are important : tensile and yield strength, toughness and soundness. The development of bolt steels has been towards better hardenability and better cold workability. Boron alloyed, relative low carbon steels have become more common as a raw material for class 8.8 bolts. An average analysis of such steels is as follows :

C	0.28 per cent
Mn	1.3 per cent
B	0.003 per cent

A small amount of chromium may also be added.

Boron steels are ideal cold forming steels for parts requiring subsequent heat treatment. By using boron it is possible to reduce the elements which influence cold forming such as Ni, Mo, Cr and above all C. A small boron addition does not adversely affect cold formability. It is worth noting that the lower Si content improves cold formability.

In order to get acceptable high strength bolts, a thorough hardening is important. Figure 5 shows the benefit of a boron steel.

With a low carbon content and a small amount of alloying elements it is possible to harden bolts up to a diameter of 23 mm. These kinds of steels are replacing chromium and molybdenium alloyed qualities to an increasing extent. The main advantages of boron steels are better forgeability, excellent combination of strength and toughness attainable and the fact that spheroidize annealing is not required.

(b) Zinc bath

The galvanizing bath used in the Zinquench process is an aluminium alloyed zinc bath. Aluminium cuts down the alloying action between the steel and the molten zinc. The absence of any appreciable zinc-iron alloy layer results in a much more ductile coating.

6.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

Because the temperature (450 °C) of the bath in the Zinquench process is very low and because no flux is used, there are no airborne, waterborne or solid wastes generated in the production process.

6.4 Specification of the emission/effluent/solid waste standards applicable in Finland

There are no official standards concerning the emission, effluent or solid waste for hot dip galvanizing plants in Finland.

6.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

No add-on pollution control measures are required for compliance with existing standards.

6.6 Specification of airborne, waterborne and solid waste discharges into the environment

There are no airborne, waterborne or solid wastes generated in the process.

6.7 Cost-related data intended to permit comparison of low- and non-waste technology with conventional technology

For comparison see 7.

7. Schematic comparison between the conventional and the low- and non-waste technology

See Figure 6.

7.6 Other significant differences between the conventional and the low- and non-waste technologies

Other significant advantages in the Zinquench process are as follows :

- continuous processing is possible
- processing time is shorter
- the need for space is less
- fewer pretreatments and rinsing operations are needed than in conventional processes

8. Reporting organization

RA-SHIPPING LTD.

9. Date of report

9 November 1979

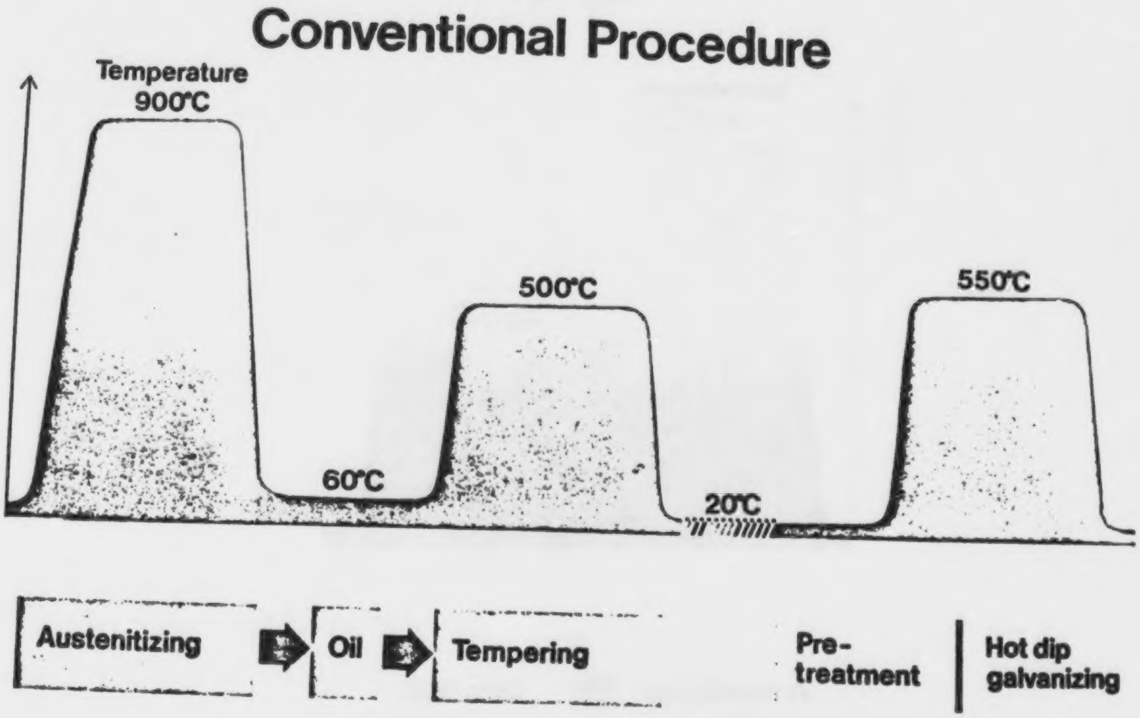
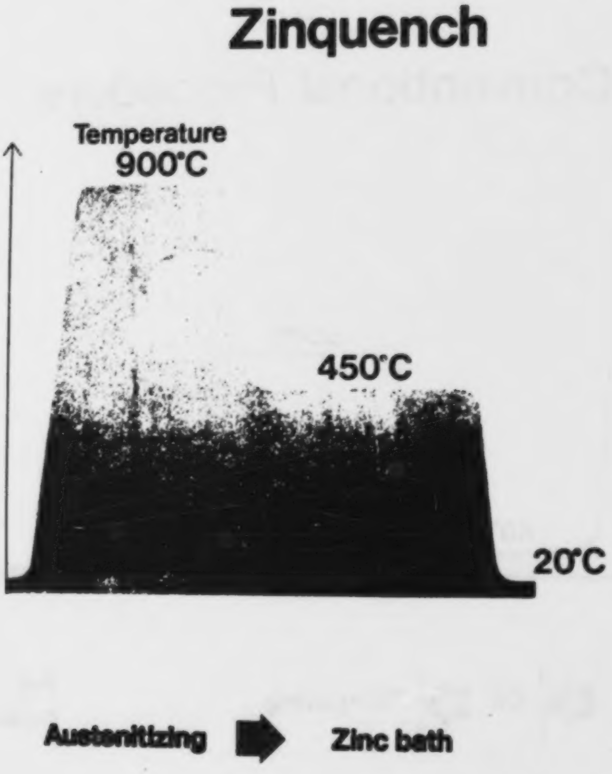

Conventional Procedure
Temperature
900°C
60°C
500°C
20°C
550°C
Austenitizing
Oil
Tempering
Pre-treatment
Hot dip galvanizing

FIG. 1



Zinquench

FIG. 2

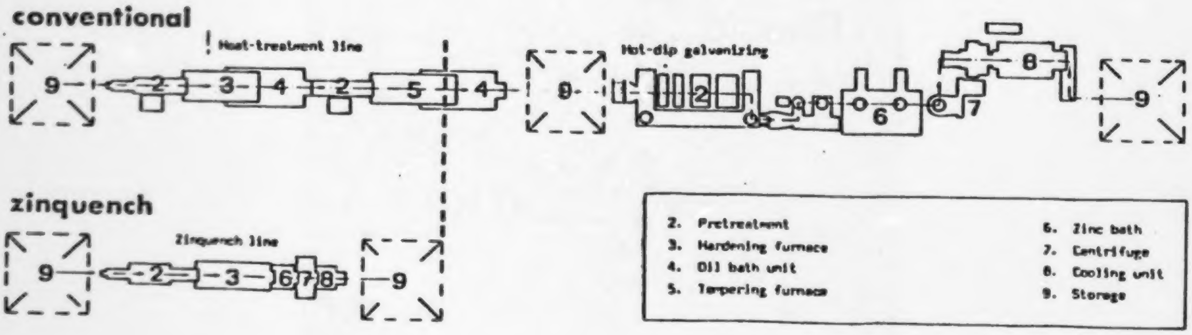
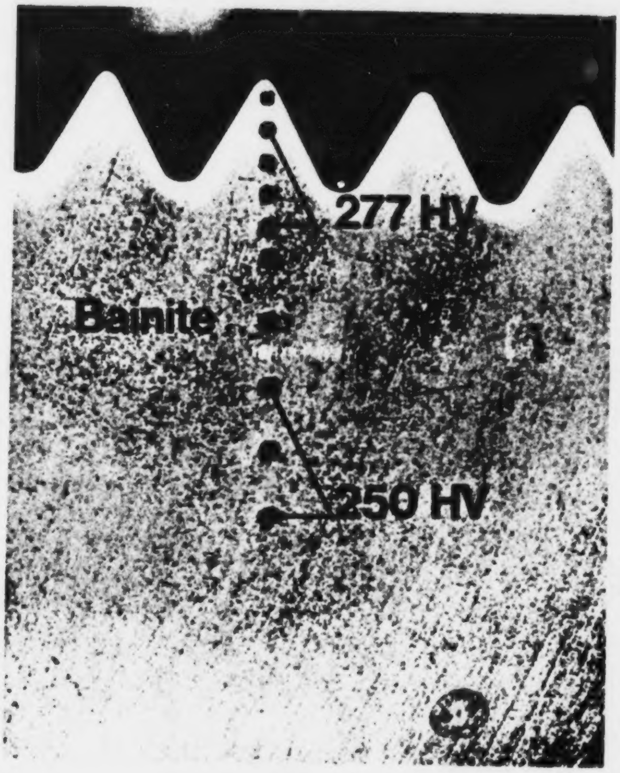

conventional
Heat-treatment line
Hot-dip galvanizing
zinquench
Zinquench line
2. Pretreatment
3. Hardening furnace
4. Oil bath unit
5. Tempering furnace
6. Zinc bath
7. Centrifuge
8. Cooling unit
9. Storage

FIG. 3

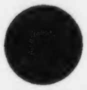


Hardness of steel

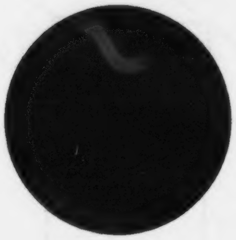
277 HV
Bainite
250 HV

FIG. 4

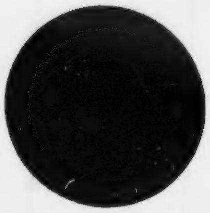
Maximum diameter of bar which can be through hardened.



BS 3111 Type 1 (DIN Cq 35)
C = 0,35%
Mn = 0,65%



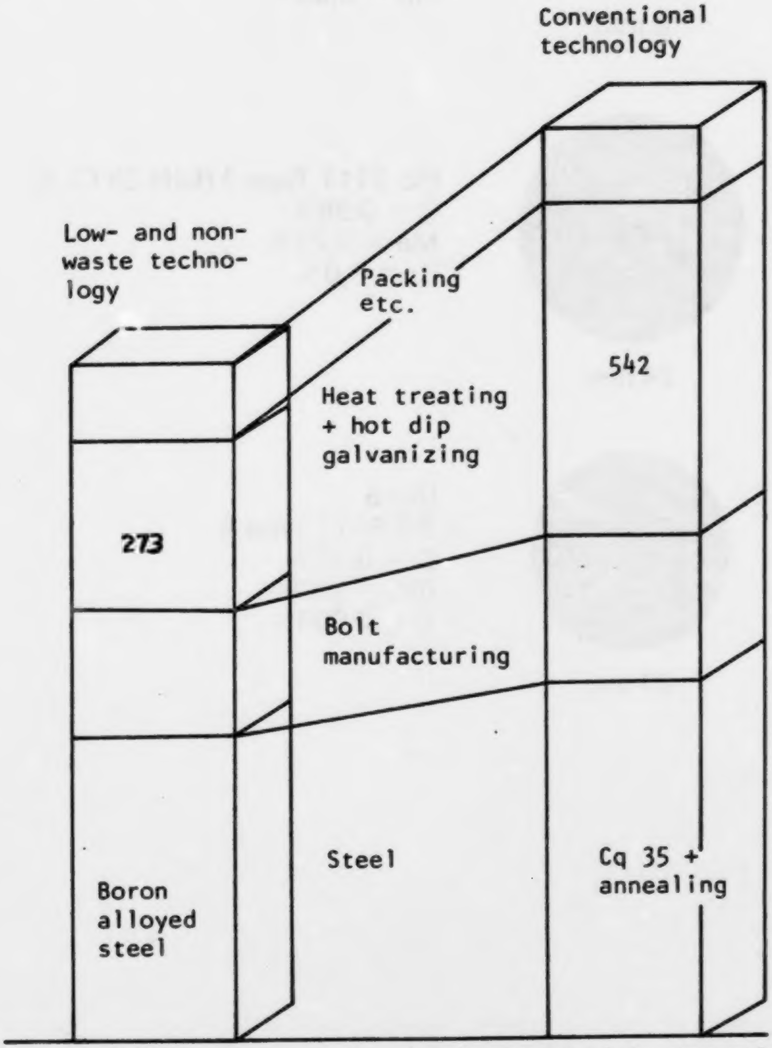
BS 3111 Type 3 (DIN 38 Cr 4)
C = 0,38%
Mn = 0,75%
Cr = 1,0%



IB 18
BS 3111 Type 9
C = 0,18%
Mn = 1,3%
B = 0,003%

FIG. 5

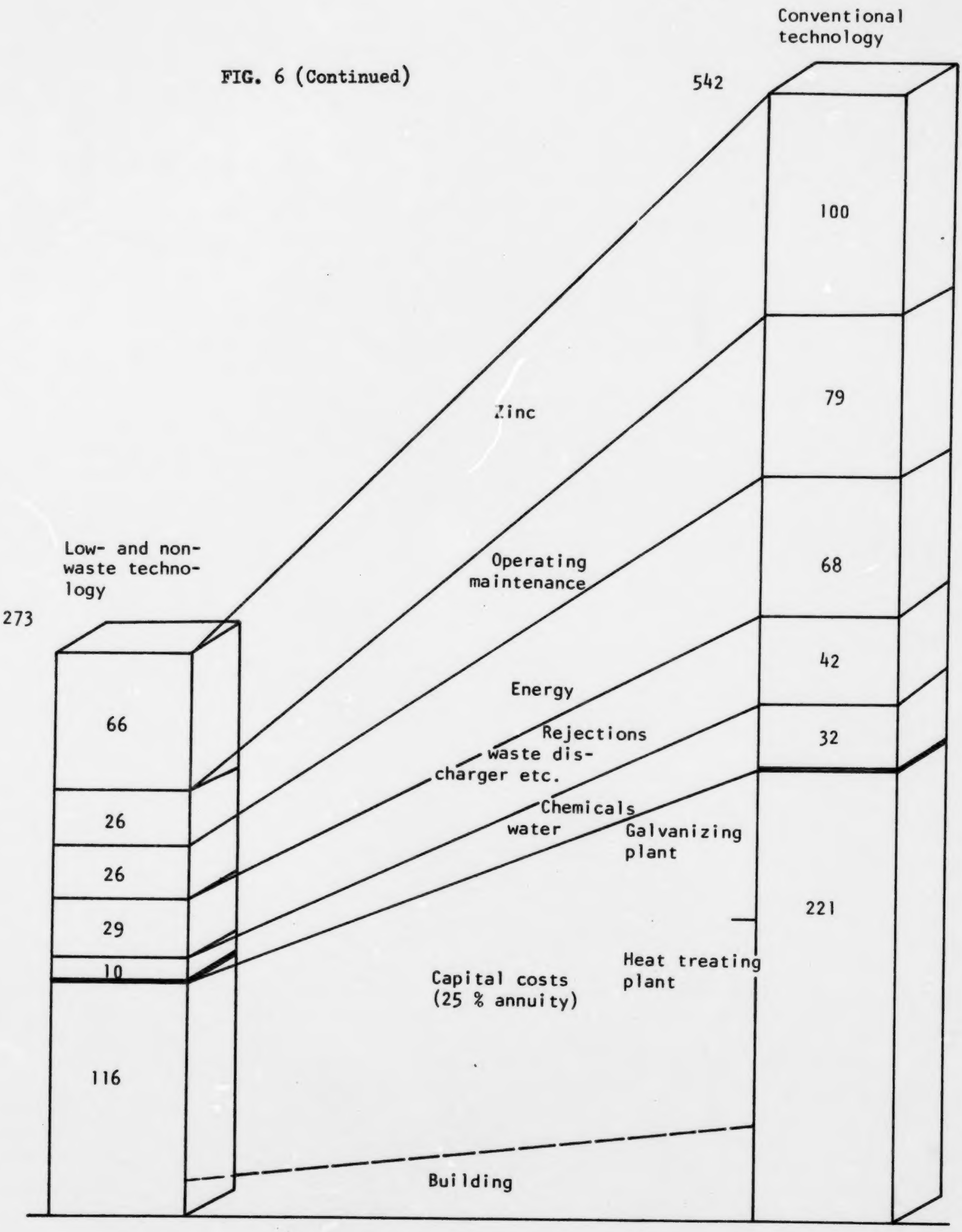
FIG. 6 SCHEMATIC COMPARISON BETWEEN THE CONVENTIONAL AND THE LOW- AND NON-WASTE TECHNOLOGY



Manufacturing costs of galvanized high strength bolts.

Figures given in US$/Mton

FIG. 6 (Continued)



Costs of heat treating and hot dip galvanizing figures given in US$/Mton

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

RESTRICTED
ENV/WP.2/5/Add.9
2 July 1981
ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

OUTOKUMPU FERRO CHROME PROCESS

Transmitted by the Government of Finland

1. Identification of industry

Ferro Chrome Production. ISIC code [1]: 3710

2. Basic characteristics of production process

Chromium raw materials are smelted in an electric furnace using coke as reductant and quartzite, dolomite, magnesite, bauxite, etc., as slag forming additives. Electric power is supplied into the furnace with three self-baking-type electrodes. Table 1 shows different production possibilities of producing ferro chrome from chromite ores.

3. Name of conventional processing technology

Production of Ferro Chrome in an open electric furnace.

4. Description of conventional processing technology

The traditional raw material for ferro chrome production has been a good, hard, lumpy ore. Due to the limited supply of these ores, FeCr-producers have been forced to use more and more low grade ores, ore fines, friable ores and even concentrates as basic raw materials. Generally ore, coke and other additives are not dried or screened before charging them into the furnace. The normal grain size distribution for feed materials in open furnace smelting process is 0-250 mm. The maximum size of the feed materials decreases when the size of the furnace decreases.

ECONOMIC
AND
SOCIAL COUNCIL

ENV/WP.2/5/Add.9
2 July 1981

ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

OUTOKUMPU FERRO CHROME PROCESS

Transmitted by the Government of Finland

1. Identification of industry

Ferro Chrome Production. ISIC code [1]: 3710

2. Basic characteristics of production process

Chromium raw materials are smelted in an electric furnace using coke as reductant and quartzite, dolomite, magnesite, bauxite, etc., as slag forming additives. Electric power is supplied into the furnace with three self-baking-type electrodes. Table 1 shows different production possibilities of producing ferro chrome from chromite ores.

3. Name of conventional processing technology

Production of Ferro Chrome in an open electric furnace.

4. Description of conventional processing technology

The traditional raw material for ferro chrome production has been a good, hard, lumpy ore. Due to the limited supply of these ores, FeCr-producers have been forced to use more and more low grade ores, ore fines, friable ores and even concentrates as basic raw materials. Generally ore, coke and other additives are not dried or screened before charging them into the furnace. The normal grain size distribution for feed materials in open furnace smelting process is 0-250 mm. The maximum size of the feed materials decreases when the size of the furnace decreases.

All feed materials are weighed and conveyed into the feeding bin of the smelting furnace. From this bin, the charge is taken to a scoop car carrying the feed into the open electric furnace. The CO-gas which is generated inside the burden is burned straight on the top of the charge by excess air. Exhaust gas is led through the hood

---

[1] International Standard Industrial Classification of Economic Activities (ENV/WP.2/5/Annex).

of the furnace, for example, to the baghouse filter. In old plants, the gas is led straight from the furnace to the atmosphere. When the gas temperature is low it has no reaction energy and has no economic value. The process diagram is shown in Figure 1 and the process gas handling systems in Figure 4.

Dust separated from the exhaust gas is normally dumped as a final waste, because it is impossible to feed it back into the smelting furnace. Special agglomeration equipment is needed if the dust is reused in the process (see Figure 7). The electric energy consumption in the open furnace smelting is high because :

- the charge is cold
- electric energy is consumed in decomposition of carbonates and hydroxides as well as evaporation of the moisture of the feed materials
- a large amount of slag is smelted if low grade ores are used

The material balance of the process is shown in Table 2 and the energy balance in Table 4. The slag quantity is generally quite high when smelting lumpy ores, because normally such ores - which would give a low slag quantity but with the right slag composition - are scarce. Several ores must be concentrated before they can be utilized in ferro chrome production. During concentrating the slag-oxides can be adjusted within certain limits to make the quality of the concentrate more suitable to the smelting process.

5. Name and state of development of low- and non-waste processing technology

The process is used commercially at Outokumpu Oy, Kemi mine, Tornio, Finland. The furnace has an annual capacity of about 50,000 tons.

6. Description of low- and non-waste processing technology

It can be presumed that the use of ore fines and concentrates is increasing because, as mentioned under point 2, the availability of high quality ores is decreasing. In addition, the increased demand for environmental protection as well as a considerable increase in energy prices have forced FeCr-producers to develop new smelting technology.

One example of these new types of processes is Outokumpu's ferro chrome smelting process, which is based on the preheating principle. The smelting of the charge is done in a totally closed electric furnace. Lumpy ore can be used in the process, which, however, has been developed for utilizing different qualities of ore fines, friable ores and concentrates, which are difficult, or even impossible, to smelt as such in an electric furnace (Figures 2 and 3).

Handling of chromium raw material comprises pelletizing and sintering of pellets in a shaft furnace. The pelletizing technology itself is conventional and has been known for several decades, but some special features have been developed for treatment of chromite raw materials. The CO-gas from the smelting furnace is used as fuel and since 1971 the coke fines from coke drying and screening have been incorporated in the pellets as additional fuel. Ready-sintered pellets, coke and flux additives are charged together into the preheating kiln. The whole charge is preheated to 1000 or 1200 °C in the kiln with the CO-gas from the smelting furnace. After preheating the gas-tight rotary feeding ring is used to feed the charge into the totally closed electric furnace. CO-gas generated in smelting is totally recovered and utilized in the processes mentioned above as well as in the coke drying kiln and in the heating of ladles. The gas handling systems of the process shown in Figure 5. All the dust separated from the gases is fed back to the process through the pelletizing plant. A considerable saving of energy has been achieved by preheating the charge, using a totally closed smelting furnace, and utilizing all the CO-gas generated in the smelting furnace.

The material balance of the process is shown in Table 3 and the energy balance in Table 4. Figure 6 shows the effect of preheating on saving electric energy in the smelting furnace.

The slag from the smelting furnace can be used :

- in casting moulds
- as base material for preparation of heat resistant castables
- as road- and railway construction material
- as insulation material in building construction.

In conventional ferro chrome smelting, using an electric furnace, waste outlets of the process are formed of the dust (450 - 1000 kg/h) when FeCr production is 50,000 t/a) in the furnace exhaust gas.

Dust is separated from the conventional electric furnace exhaust gases with bag-house filters. The separation efficiency of the filters is now excellent, and the airborne amount is lower than 20 mg/Nm^3 gas. Because the heat resistance of the bag filter cloth is limited, the furnace gas is cooled down by mixing in air in considerably high quantities before leading it to the filter. Therefore, the size of the filter is big, and the total gas quantity cleaned from 270,000 to 400,000 Nm^3/h (44,000 to 66,000 Nm^3/t FeCr).

The treatment of very fine separated dust causes environmental troubles. Normally the dust is dumped and considerable Cr-losses take place (Cr_2O_3 - content of the dust is 30 to 45 per cent).

The slag quantity in conventional ferro chrome smelting is 1.3 to 1.7 ton slag per ton of metal.

Figure 4 shows the gas handling systems of the open electric furnace and the wastes generated in the process.

When using a closed electric furnace for FeCr-smelting a preheated or cold charge can be used. The CO-content of furnace gas is 80 to 90 per cent.

Because of the highly flammable nature of the gas, normally venturi scrubbers are used for gas cleaning. After cleaning, the CO-gas is totally used as fuel and no harmful airborne waste is produced.

Heat values of closed furnace gas

Furnace gas (298°k)	A	B
CO	80 per cent	90 per cent
H_2	3	3.5
H_2O	5	2
CO_2	7	2.5
N_2	5	2
Exhaust gas (500°k)		
CO_2	34 per cent	34 per cent
H_2O	3	2
N_2	63	64
O_2	-	-
HEAT VALUE	2.68 kWh/Nm^3	3.03 kWh/Nm^3

Heat values of the gas from the closed electric furnace

The dust and the water soluble components pass into the washing water. The water amount used for cleaning is 1.5 to 5 m^3/MWh, depending on the type of scrubber.

The waste waters are led to the settling basins, where the solid material recovery is 94 to 98 per cent. The dust separated is fed back to the process through the pelletizing plant.

If the closed electric furnace is working with a preheated charge, part of the CO-gas is used in the kiln as fuel. The rest of the CO-gas can be utilized totally in other stages of the process (see Figure 3). The exhaust gas from the kiln is first cleaned in a dry cyclone and the dust thus separated is fed to the pelletizing plant. In the second cleaning stage, a venturi scrubberis used. The separation capacity of the cleaning is over 99 per cent. The dust-laden washing water is led to the same settling basins as the washing water from the smelting furnace. In a process like this, no dust dumping problems arise as the dusts separated are fed back to the process through the pelletizing plant. Figure 5 shows the gas handling systems and the wastes generated in the process.

In the above text, special attention has been paid to different types of airborne, waterborne and solid wastes. Noise level is also an environmental problem. Around the open electric furnace the noise level of 85 dB(A) is exceeded. The roof of the closed electric furnace prevents very well the emission of noise generated in the smelting operation, lowering the noise level always to less than 85 dB(A).

The Ministry of Social Affairs and Health in Finland has published some recommendations for the maximum limits for different wastes in air. The laws for environmental protection are being updated.

Regulations concerning water protection and treatment of solid wastes are stipulated in water laws and in laws for waste service. These laws, however, do not give any common standards for the whole country or for a certain branch of industry. For waste waters, the authorities specify the maximum limits for different wastes, case by case. They have specified the maximum limit for solids in waste waters led into open water. This limit is 100 mg/l.

Plans for the treatment of solid wastes must be submitted to the authorities before start-up of a plant. There are, however, no special standards for solid waste treatment.

Nowadays, the Finnish authorities require regular checking of waste waters and the quality of the surrounding water into which waste waters are fed. This must be done, even if no limits have been set. The checking is done either with automatic sampling equipment or by taking individual samples at certain intervals.

7. Schematic comparison between the conventional and the low- and non-waste technology

The basic information for comparison is as follows :

	Open furnace (conventional)	Closed furnace (new technology)
Product	Ferro chrome (Charge grade)	Ferro chrome (Charge grade)
Capacity	50,000 t/a	50,000 t/a
Process	Ferro chrome smelting in an open electric furnace. Lumpy ore is used as basic raw material.	Ferro chrome smelting in a closed electric Chrome concentrate as pelletized raw material is used. The whole charge is preheated before smelting.
Operating days/ year	8,322 h/a (95%)	8,322 h/a (95%)
Location	A calculated example based on existing works.	Tornio, Finland
Year used in this report	1979	1979

Further information on this comparison is presented in the following Figures and Tables

- Material balances	Tables 2 and 3
- Energy balances	Table 4
- Other facts about differences in raw materials, process operation, costs, etc.	Figures 2 and 3; Tables 5 and 6
- Gas handling systems and wastes generated	Figures 4 and 5; Table 5

8. Identification of needs for further research and development with regard to the low- and non-waste technology

The process metallurgy of ferro chrome smelting by using different types of raw materials is now well-known. Further research and development, however, is necessary to find ways to produce ferro chrome that are even more economical in terms of material and energy savings and that are less polluting. When laws for environmental protection are tightening controls, special attention must be paid to gas and dust handling systems. Figure 7 presents dust handling technology for open electric furnaces obtainable today. In the future, the venturi scrubbers in closed electric furnaces will, in all probability, be changed to dry cleaning equipment, and the heat content of gas will be recuperated in a heat exchanger.

The flowsheet of the future ferro chrome smelting process is shown in Figure 8. This process, developed and patented by Outokumpu Company, has been tested on a full scala, but it is not working continuously yet. Some stages of the process are still under development. A brief description of the process is as follows : Ore fines or concentrate is fed with coke fines and some additives into a rotary kiln, where feed is agglomerated to bigger lumps, and prereduced. The prereduced material, at a temperature above 1400 °C, is then fed to special feeding equipment, where coarse coke and fluxes are mixed and preheated before the whole charge is fed hot into the totally closed electric furnace. CO-gas formed inside the burden is recovered and used as fuel in prereduction and preheating furnaces.

In this process the electric energy consumption can be reduced by 100 or 400 kWh/t FeCr (depending on the prereduction degree) from the figures achieved today by using preheated charge in the closed electric furnace. Also, dry dusts separated from various process stages can be totally fed back to the beginning stage of the process.

9. Reporting organization

Outokumpu Oy, P.O.B. 27, 02201 Espoo 20, Finland.

10. Date of report

17 January 1980

COMPARISON BETWEEN THE CONVENTIONAL AND LOW - AND NON - WASTE FeCr-SMELTING TECHNOLOGY

FIG. 1. OPEN FURNACE

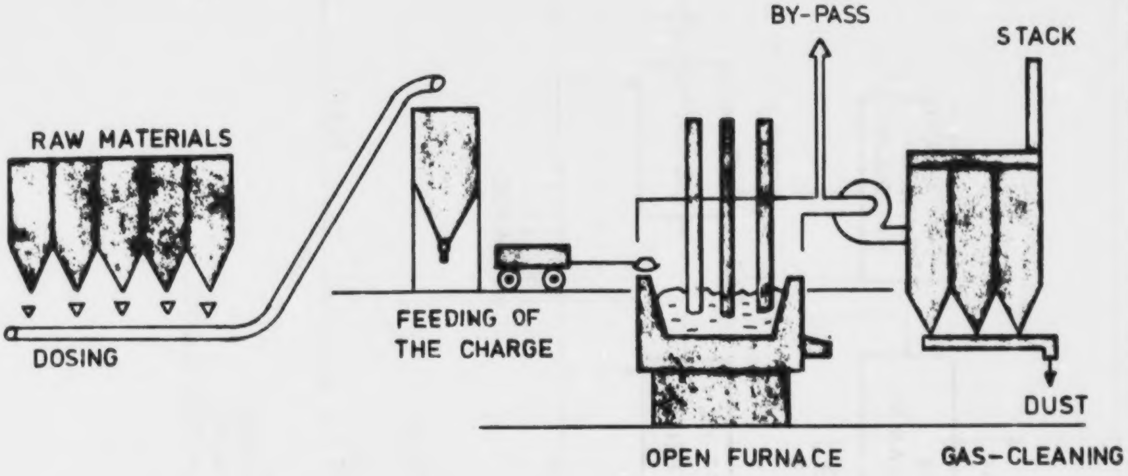
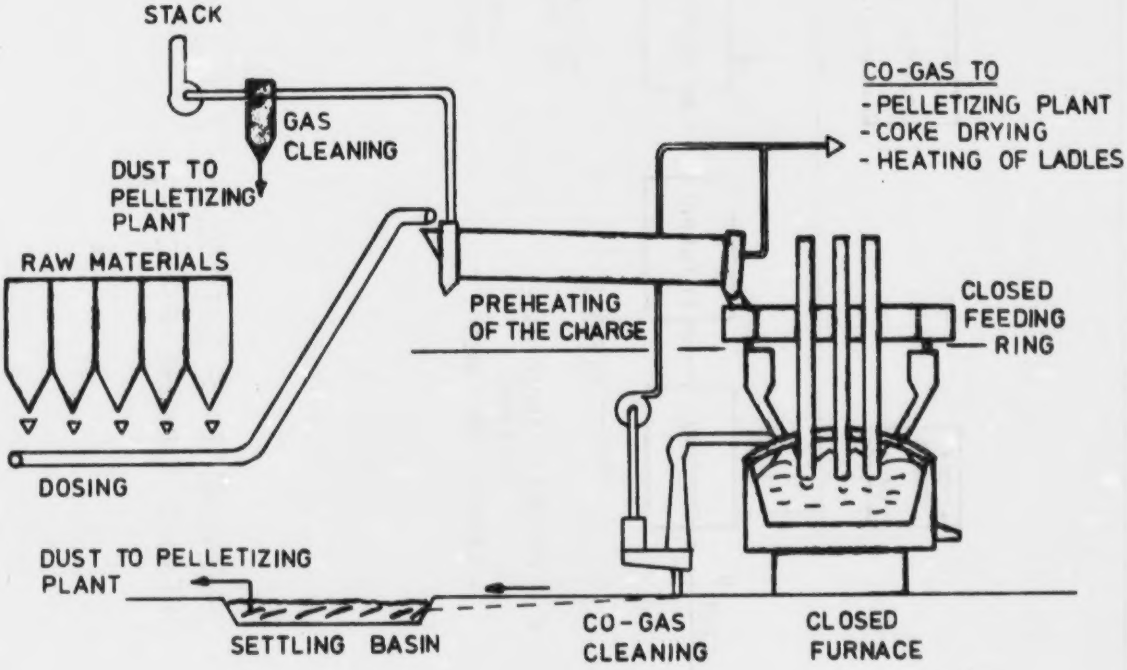
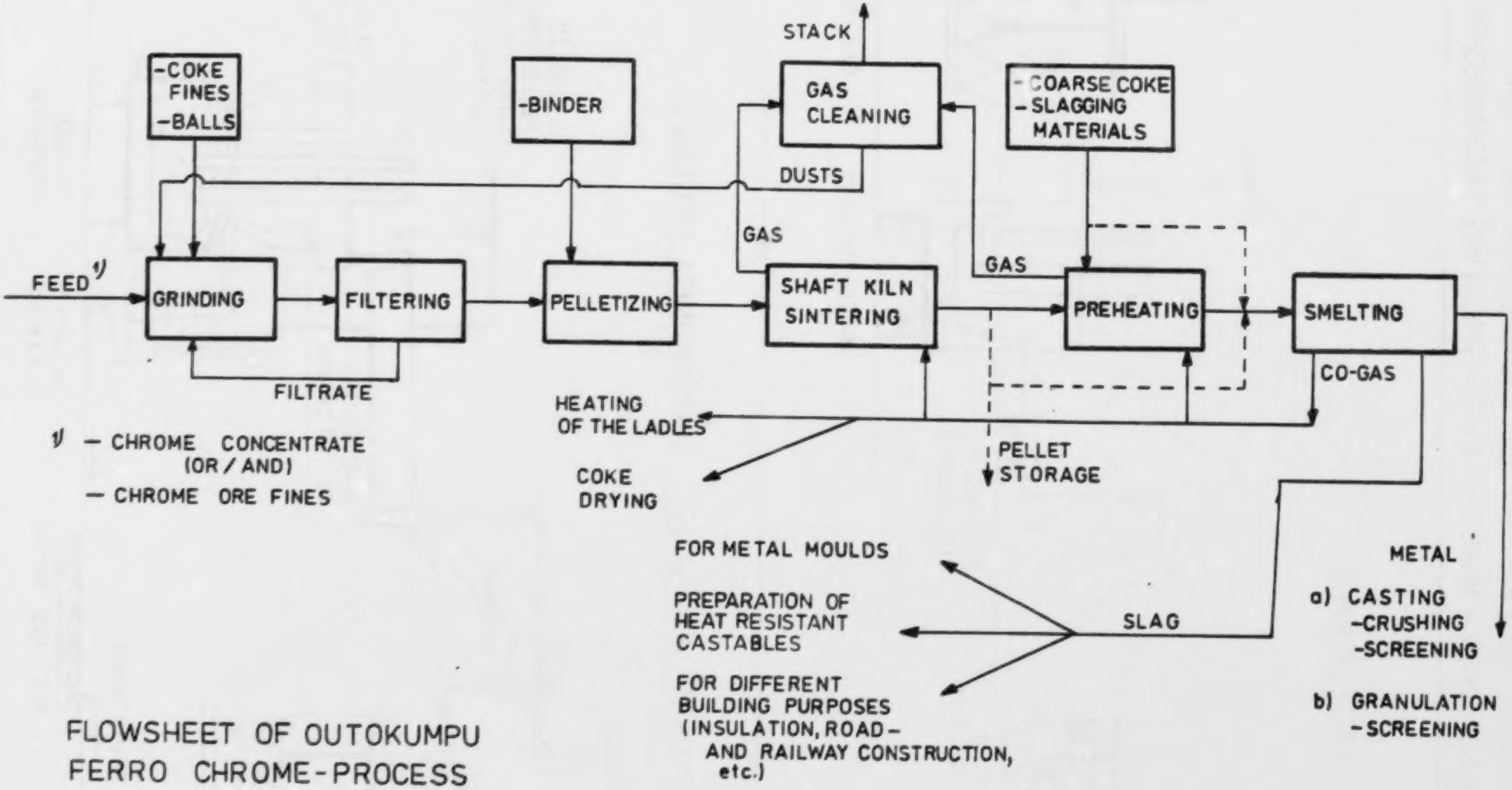

BY-PASS
STACK
RAW MATERIALS
DOSING
FEEDING OF THE CHARGE
DUST
OPEN FURNACE
GAS-CLEANING

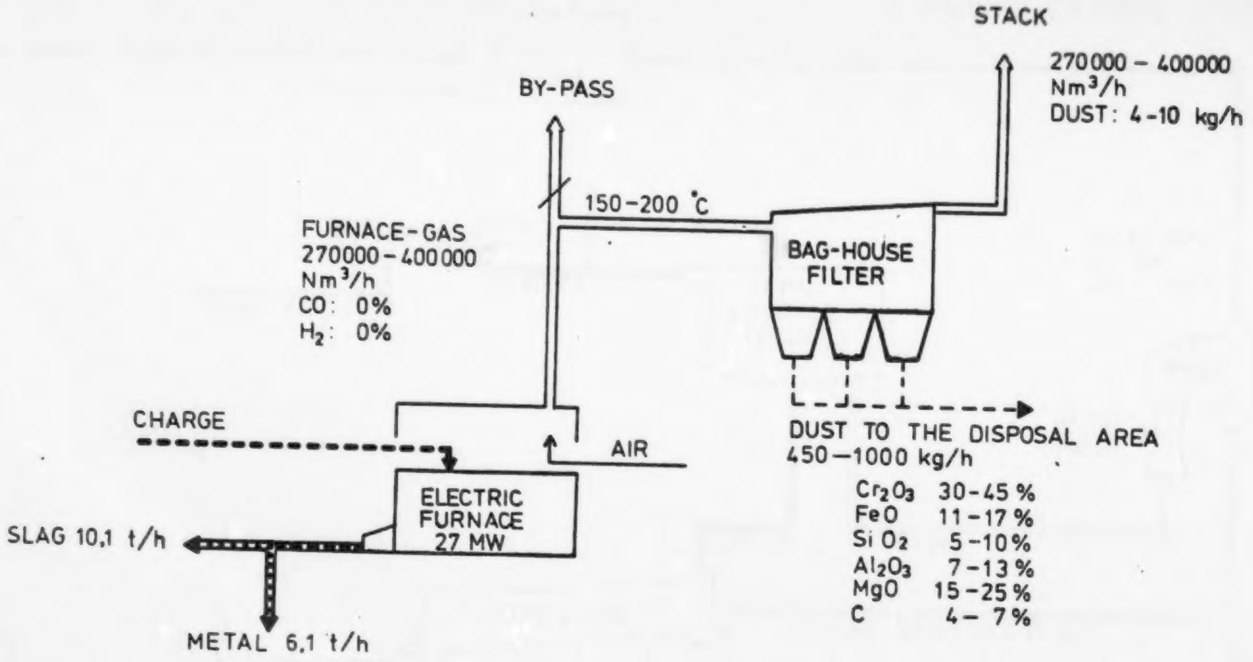
FIG. 2. CLOSED FURNACE (OUTOKUMPU PROCESS)


STACK
GAS CLEANING
DUST TO PELLETIZING PLANT
CO-GAS TO
- PELLETIZING PLANT
- COKE DRYING
- HEATING OF LADLES
RAW MATERIALS
PREHEATING OF THE CHARGE
CLOSED FEEDING RING
DOSING
DUST TO PELLETIZING PLANT
SETTLING BASIN
CO-GAS CLEANING
CLOSED FURNACE


-COKE
FINES
-BALLS
-BINDER
STACK
GAS
CLEANING
-COARSE COKE
-SLAGGING
MATERIALS
DUSTS
GAS
GAS
FEED 1)
GRINDING
FILTERING
PELLETIZING
SHAFT KILN
SINTERING
PREHEATING
SMELTING
FILTRATE
CO-GAS
HEATING
OF THE LADLES
COKE
DRYING
PELLET
STORAGE
1) - CHROME CONCENTRATE
(OR / AND)
- CHROME ORE FINES
FOR METAL MOULDS
PREPARATION OF
HEAT RESISTANT
CASTABLES
FOR DIFFERENT
BUILDING PURPOSES
(INSULATION, ROAD-
AND RAILWAY CONSTRUCTION,
etc.)
SLAG
METAL
a) CASTING
-CRUSHING
-SCREENING
b) GRANULATION
-SCREENING

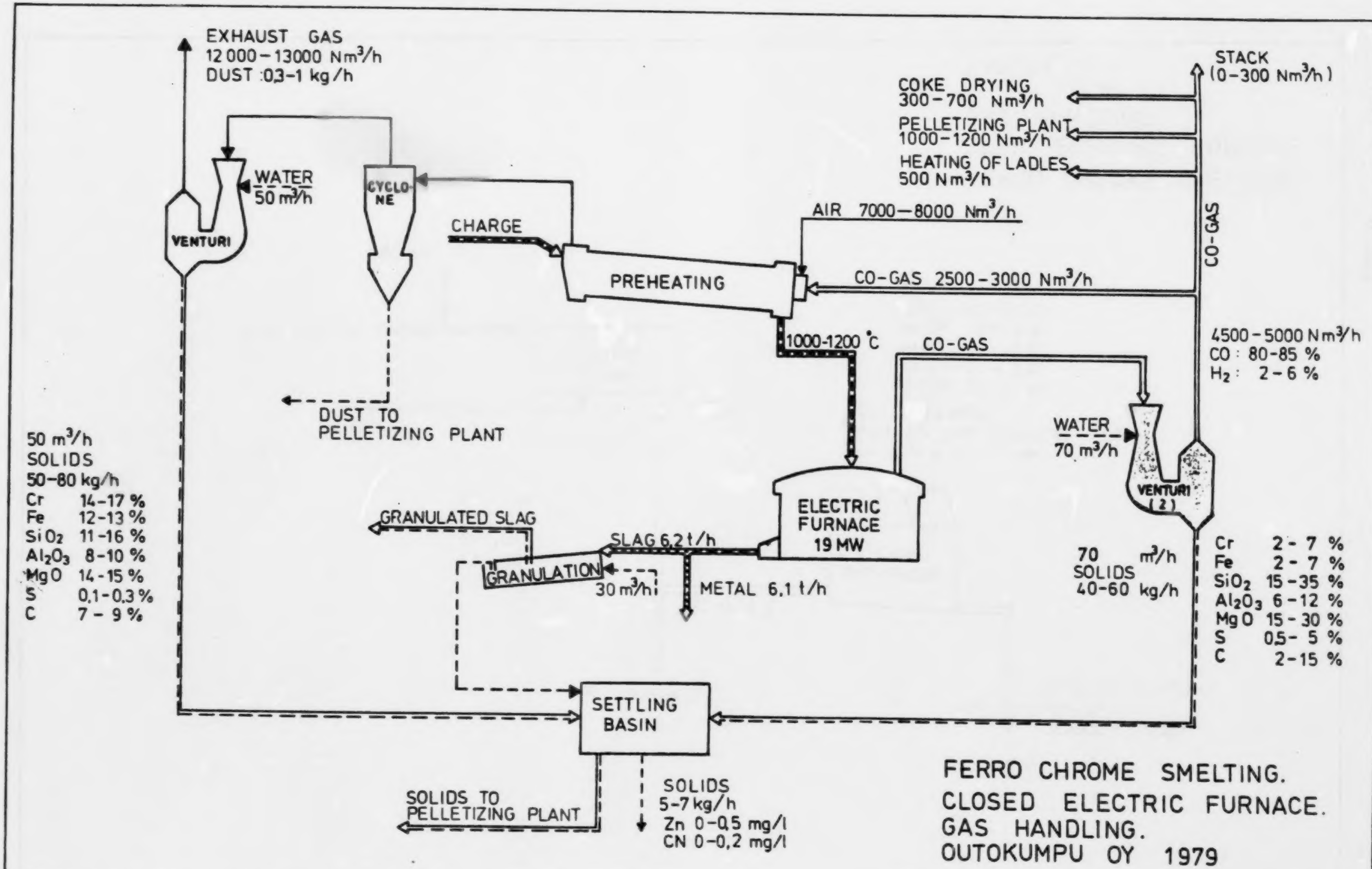
FLOWSHEET OF OUTOKUMPU
FERRO CHROME-PROCESS

FIGURE 3


STACK
270000 - 400000
Nm³/h
DUST: 4-10 kg/h
BY-PASS
150-200 °C
BAG-HOUSE FILTER
FURNACE-GAS
270000-400000
Nm³/h
CO: 0%
H₂: 0%
CHARGE
AIR
ELECTRIC FURNACE 27 MW
SLAG 10,1 t/h
METAL 6,1 t/h
DUST TO THE DISPOSAL AREA
450–1000 kg/h
Cr₂O₃ 30-45 %
FeO 11-17 %
SiO₂ 5-10%
Al₂O₃ 7-13 %
MgO 15-25 %
C 4- 7 %

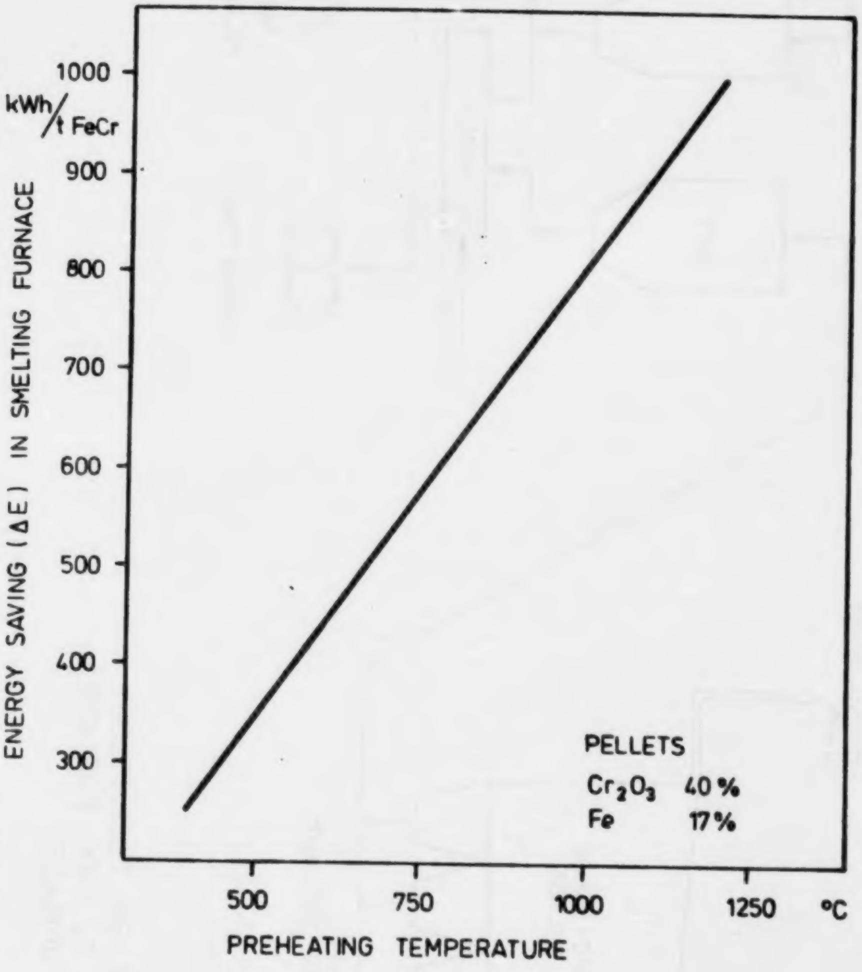
FERRO CHROME SMELTING.
OPEN ELECTRIC FURNACE.
GAS HANDLING.

FIGURE 4


EXHAUST GAS
12 000 – 13000 Nm³/h
DUST :0,3-1 kg/h
WATER
50 m³/h
VENTURI
CYCLONE
CHARGE
PREHEATING
AIR 7000—8000 Nm³/h
CO-GAS 2500-3000 Nm³/h
STACK
(0-300 Nm³/h)
COKE DRYING
300-700 Nm³/h
PELLETIZING PLANT
1000-1200 Nm³/h
HEATING OF LADLES
500 Nm³/h
CO-GAS
1000-1200 °C
CO-GAS
4500-5000 Nm³/h
CO : 80-85 %
H2 : 2-6 %
WATER
70 m³/h
VENTURI (2)
DUST TO
PELLETIZING PLANT
50 m³/h
SOLIDS
50-80 kg/h
Cr 14-17 %
Fe 12-13 %
SiO2 11-16 %
Al2O3 8-10 %
MgO 14-15 %
S 0,1-0,3 %
C 7 - 9 %
ELECTRIC FURNACE 19 MW
GRANULATED SLAG
SLAG 6,2 t/h
GRANULATION
30 m³/h
METAL 6,1 t/h
70 m³/h
SOLIDS
40-60 kg/h
Cr 2 - 7 %
Fe 2 - 7 %
SiO2 15 - 35 %
Al2O3 6 - 12 %
MgO 15 - 30 %
S 0,5 - 5 %
C 2 - 15 %
SETTLING BASIN
SOLIDS TO
PELLETIZING PLANT
SOLIDS
5-7 kg/h
Zn 0-0,5 mg/l
CN 0-0,2 mg/l

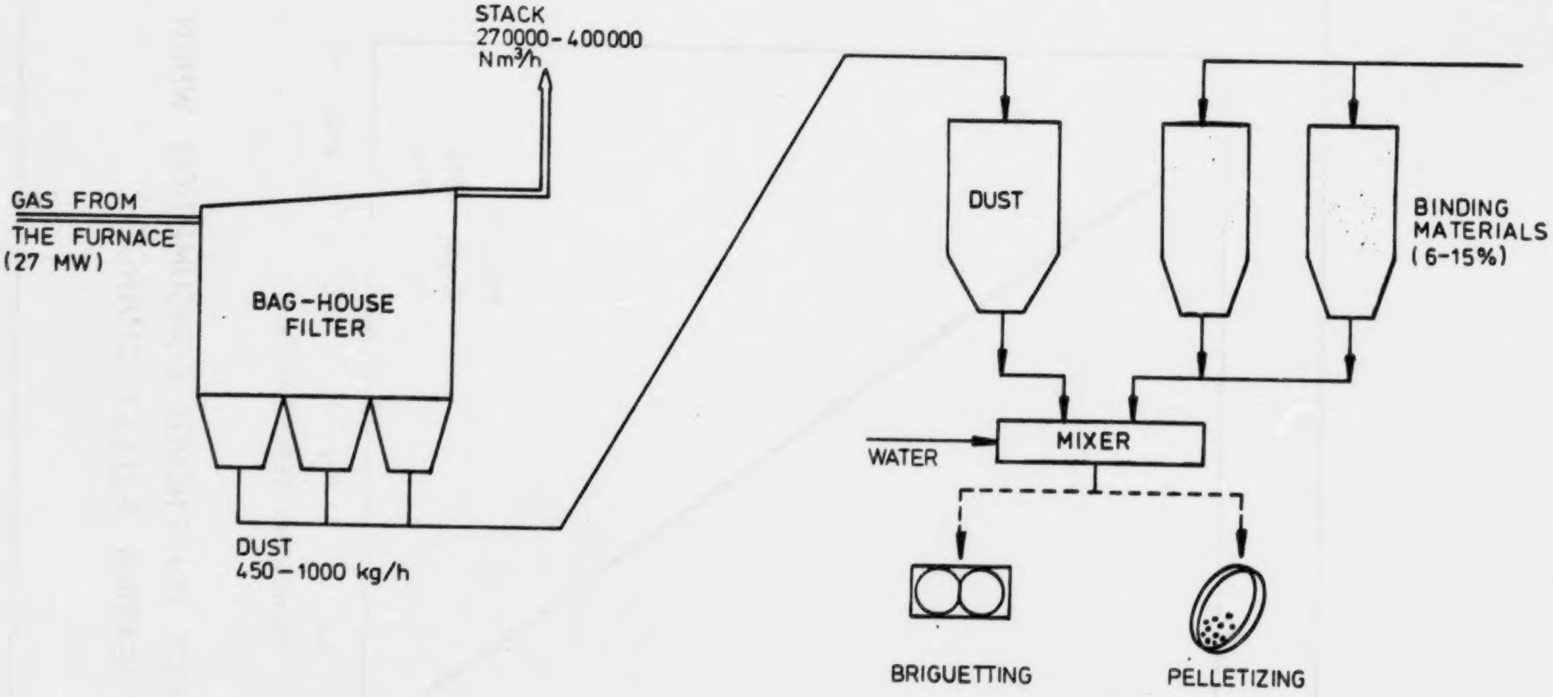
FERRO CHROME SMELTING.
CLOSED ELECTRIC FURNACE.
GAS HANDLING.
OUTOKUMPU OY 1979

FIGURE 5



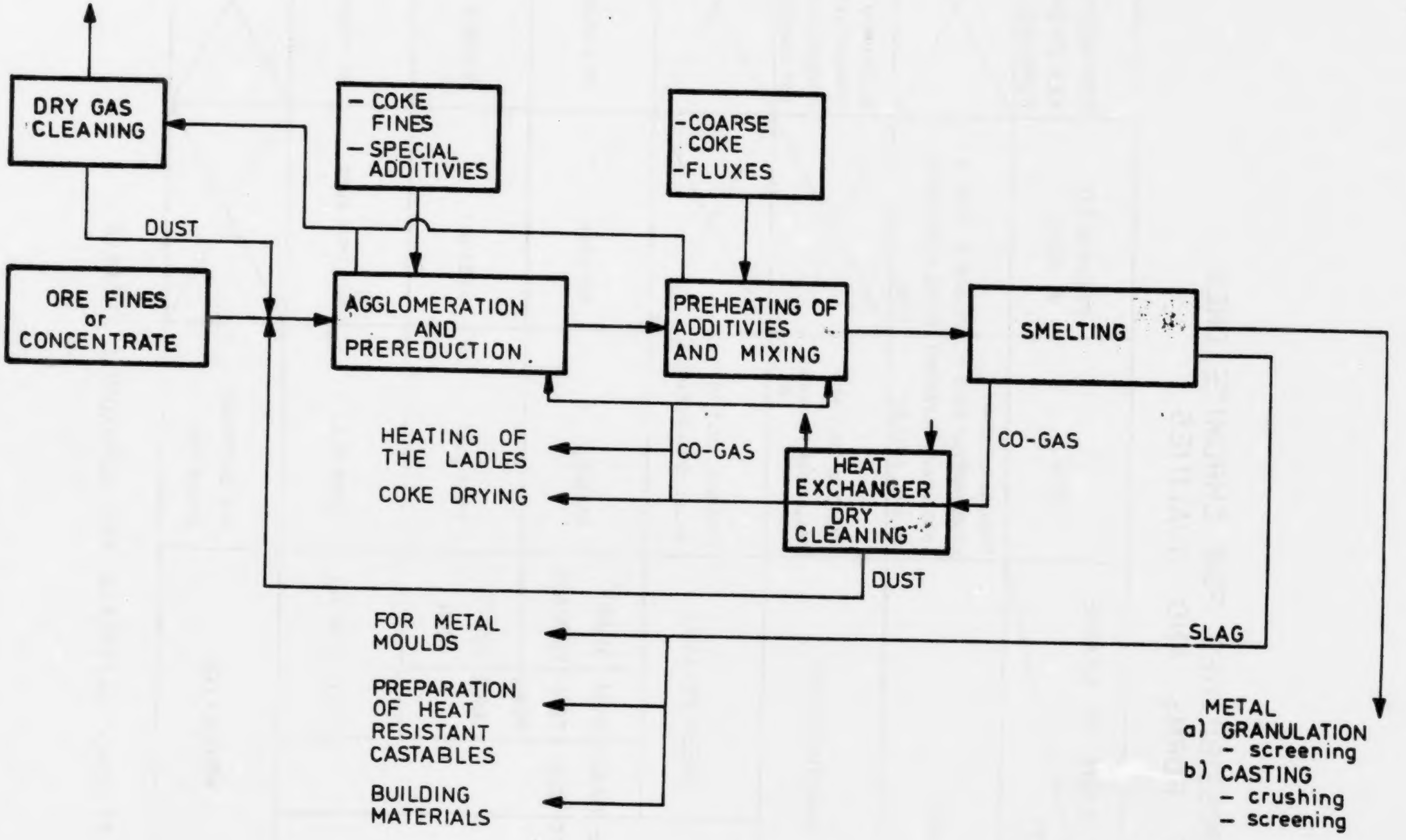
EFFECT ON ENERGY CONSUMPTION WHEN PREHEATING PELLET CHARGE

FIGURE 6


STACK
270000-400000
Nm³/h
GAS FROM
THE FURNACE
(27 MW)
BAG-HOUSE
FILTER
DUST
450-1000 kg/h
DUST
BINDING
MATERIALS
(6-15%)
WATER
MIXER
BRIGUETTING
PELLETIZING

DUST HANDLING TECHNOLOGY OBTAINABLE TO DAY FOR OPEN ELECTRIC FURNACES.

FIGURE 7.


DRY GAS CLEANING
DUST
ORE FINES or CONCENTRATE
- COKE FINES
- SPECIAL ADDITIVIES
AGGLOMERATION AND PREREDUCTION.
-COARSE COKE
-FLUXES
PREHEATING OF ADDITIVIES AND MIXING
SMELTING
CO-GAS
CO-GAS
HEATING OF THE LADLES
COKE DRYING
HEAT EXCHANGER
DRY CLEANING
DUST
FOR METAL MOULDS
PREPARATION OF HEAT RESISTANT CASTABLES
BUILDING MATERIALS
SLAG
METAL
a) GRANULATION
- screening
b) CASTING
- crushing
- screening

FLOWSHEET OF THE FUTURE FERRO CHROME PROCESS.
OUTOKUMPU OY

FIGURE 8

TABLE 1

PRODUCTION POSSIBILITIES FOR CHROMITE ORES OF DIFFERENT FORMS AND QUALITIES

FORM AND QUALITY / STATE OF CHARGE						COLD	PREHEATED IN KILN	PREREDUCED IN KILN OR SPEC. FURNACE
LUMPY						POSSIBLE. ENERGY CONSUMPTION 3800 – 4500 kWh/t DEPENDING ON ORE QUALITY	POSSIBLE WITH A SIZED HARD LUMPY ORE	☒
CONCENTRATE	NOT AGGLOMERATED					POSSIBLE ONLY IN SMALL OPEN FURNACES	☒	OUTOKUMPU OY'S CONCENTRATE PROCESS PROCESS DEVELOPMENT NOT FINISHED
	AGGLOMERATED	PELLETS	GREEN PELLETS			POSSIBLE ONLY IN SMALL OPEN FURNACES	☒	☒
			HARDENED	HIGH TEMPERATURE	SHAFT FURNACE	POSSIBLE	POSSIBLE	NO EXPERIENCE
					GRATE-KILN	POSSIBLE	POSSIBLE	POSSIBLE
				COLD BONDING		POSSIBLE	NO EXPERIENCE	NO EXPERIENCE
		BRIQUETTES				NOT SUFFICIENT STRENGTH	☒	☒

☐ ACTUAL FEEDING MATERIALS FOR OUTOKUMPU PROCESS

TABLE 2

MATERIAL BALANCE, OPEN ELECTRIC FURNACE

	FEEDS				PRODUCTS		
	LUMPY ORE I	LUMPY ORE II	COKE	QUARTZITE	METAL	SLAG	DUST
KG a/	2335	778	457	137	1000	1650	75
ANALYSE %							
Cr	19.5	21.4	0.1	0.08	54.6	4.4	23
Fe	11.7	10.7	0.7	0.4	34.1	1.3	13
C			90		7.7		5
S	0.007		0.65	0.018			
P	0.004		0.021	0.004			
SiO_2/Si	16.7	7.2	5.0	97	2.9	30.4	10
Al_2O_3/Al	10.2	26.5	2.6	0.9		26.3	8
MgO/Mg	18.9	15.8	0.2	0.08		31.8	20
CaO/Ca	2.3	0.9	0.3	0.06		3.5	1
Ash			9.3				
VOLATILES			0.7				

a/ Calculated kg/t smelted metal)

TABLE 3

MATERIAL BALANCE, CLOSED ELECTRIC FURNACE

	FEEDS				PRODUCTS		
	PELLETS	COKE	QUARTZITE	DOLOMITE	METAL	SLAG	DUST
KG a/	2100	460	200	165	1000	1017	8
ANALYSE %							
Cr	28.1	0.1	0.08		52.0	6.2	5
Fe	18.4	0.7	0.4	1.3	36.5	2.6	5
C		90			7.4		5
S	0.007	0.65	0.018	0.022	0.043	0.18	3
P	0.002	0.021	0.004	0.031	0.014	0.001	
SiO_2/Si	6.8	5.0	97	9.0	2.9	28.6	25
Al_2O_3/Al	12.6	2.6	0.9	2.0		26.4	8
MgO/Mg	12.5	0.2	0.08	18.2		26.7	20
CaO/Ca	0.8	0.3	0.06	27.3		5.8	3
Ash		9.3					
VOLATILES		0.7					

a/ Calculated kg/t smelted metal)

TABLE 4

ENERGY BALANCES. SMELTING FURNACE.
(KWH/T SMELTED FERRO CHROME)

	OPEN ELECTRIC FURNACE (COLD CHARGE)	CLOSED ELECTRIC FURNACE (CHARGE 1000°C)
IN		
FEED	0.0	854.5
SLAG FORMATION	208.4	131.6
CARBIDE FORMATION	62.4	55.3
REACTIONS OF CARBON	2758.8	2908.2
ELECTRIC ENERGY	4113.8	2469.3
TOTAL	7143.4	6418.9
OUT		
METAL	419.9	417.0
SLAG	1368.4	812.7
EXHAUST GAS + DUSTS	280.4	304.5
REDUCTION	2461.3	2552.4
DECOMPOSITIONS AND WATER EVAPORATION	216.6	0.0
FURNACE GAS REACTION ENERGY	1984.8	2092.3
LOSSES	412.0	240.0
TOTAL	7143.4	6418.9

TABLE 5

COMPARISON BETWEEN THE OPEN- AND CLOSED ELECTRIC FURNACE FERRO CHROME SMELTING TECHNOLOGY

	Open furnace (Conventional)	Closed furnace (New technology)	Difference
Raw materials (See also tables II and III)	When 50000 t FeCr/a produced, the following raw materials are used. (Dry weights): Lumpy ore 162136 t/a Coke 23802 t/a Quartzite 7135 t/a Dolomite -	When 50000 t FeCr/a produced, the following raw materials are used. (Dry weights): Pellets 109323 t/a Coke 23958 t/a Quartzite 10417 t/a Dolomite 8594 t/a	
	Raw materials are normally unscreened and moist	Coke is dried and screened. Coke fines is used as fuel in the pelletizing process. Fluxes are used as screened.	
	Electrode paste consumption is 20-25 kg/t FeCr, due to the moisture of the charge and to the fines, which are channeling the gases around the electrodes.	Electrode paste consumption is 9-11 kg/t FeCr. H_2-content and gas amount is low. Gas penetration is even, because of the even sized charge. Unit energy consumption is lower.	Electrode paste cons. 9-14 kg lower in the closed electric furnace.
Energy (See also table IV)	Energy cons. kWh/t FeCr Dosing 7 Gas cleaning 256 Smelting 4285 Miscellanous 43 TOTAL 4591	Energy cons. kWh/t FeCr Dosing/preheating 25 Gas cleaning 27 Smelting 2573 Miscellanous 48 TOTAL 2673	In smelting operation 1918 kWh/t FeCr more electric energy is used in open furnace.
	When produce 50000 t FeCr/a a transformer capacity of 33 MVA is needed.	When produce 50000 t FeCr/a a transformer capacity of 22 MVA is needed.	Transformer capacity must be 50 % higher in open furnace.
	No preheating of charge is used.	Whole charge is preheated 1000-1200°C with electric furnace gas. Preheating temperature versus energy savings is presented in the figure 6.	

Table 5 (continued)

	OPEN FURNACE	CLOSED FURNACE	DIFFERENCE
Waste discharges (See also figures 4 and 5) FeCr-production 50000 t/a	Gases: 270000-400000 Nm^3/h gas is cleaned. In older plants no gas cleaning is done. Solid wastes: dusts - airborne 35-80 t/a - waterborne - t/a - dumping 4000-8500 t/a slag 84000 t/a	Gases: Furnace gas (4500-5000 Nm^3/h) is cleaned and used totally as fuel. Gas amount from the preheating furnace is 12000-13000 Nm^3/h. It is cleaned. Solid wastes: dusts - airborne 3-9 t/a - waterborne 40-60 t/a - dumping - t/a slag 52000 t/a	Because of the relative high amount of gases treated in the open furnace smelting, the gas cleaning system is 200% more expensive, than in the closed furnace smelting (see also table VI).
Investment and production costs (See also table VI)	Relative investment 100 Production costs see table VI.	Relative investment 130 Production costs are 48,0 US dollars/t FeCr less than in the open furnace (see table VI).	Total extra production cost in the open furnace is 2,4 mil. US dollars/a. (See also table VI)
Other areas for comparison. Smelting operation	The charge is smelted in an open furnace which is lined with carbon blocks and/or refractory bricks. Due to the unclassified feed, the distribution of gases in the burden is ununiform. A stoking machine is needed to keep the charge unsintered or to prevent gas blows or eruptions. Open furnace has a high noise level. Electrode protection by cooling is necessary. The maintenance problems of the electrodes are difficult. The gas oxidizes by air immediately on the surface of the burden. The temperature of the gas is low and it has no economical value. The volume of the exhaust gas is 10-15 Nm^3/kWh.	The smelting furnace is similar to the conventional furnace but it is covered by a roof made of refractory castables and bricks. The roof is partly water cooled. The porosity of the charge allows an uniform and free distribution of reduction gas through the charge. No stoking machine is necessary. Uniform gas distribution and the roof of the furnace give a low noise level at the furnace. Electrode protection isn't necessary. The gas amount from the closed furnace is low and its reaction energy is high because it is not oxidized. The volume of the exhaust gas is 0.2-0.3 Nm^3/kWh. The exhaust gas is utilized as fuel in the preheating furnace etc. (see figures 3 and 5).	

Table 5 (continued)

	OPEN FURNACE	CLOSED FURNACE	DIFFERENCE
Tapping	Tapping is taken every 1-3 hour and up to 4 tapping holes are needed because the unscreened material causes an ununiform molten metal distribution.	Tapping is taken every second hour. Only one tapping hole is needed because of a uniform charge and furnace operation.	
Casting of the metal	The metal is generally cast into the metal moulds. The cost of casting when using metal moulds is considerable high.	The metal is cast into the moulds made of granulated slag or screened FeCr-fines. The water granulation of the metal is also possible.	
Slag treatment	Slag is dumped and has normally no economical value. Slag treatment needs much manpower.	The slag is granulated in the water. Slag is used for the preparation of the heat resistant castables and for different building purposes (Insulation material, for road- and railway construction etc.)	

TABLE 6

COMPARISON OF THE PRODUCTION COSTS (1 US $ = 3,75 FIM)

	OPEN FURNACE			CLOSED FURNACE			DIFFERENCE
Production costs	Cons./t FeCr	Unit cost	cost/t FeCr	Cons./t Fecr	Unit cost	cost/t FeCr	
- Raw materials							Other production costs not mentioned in the table are equal in both cases.
- Lumpy ore	3,3	58	191,4	-	-	-	
- Concentrate	-	-	-	2,2	79	173,8	
- Coke drying and pelletizing of the concentrate	-	-	-	-	-	41,5	
- Extra fluxes	-	-	-	-	-	2,5	
- Electric energy	4591 kWh	32 mills	147,0	2673 kWh	32 mills	85,6	The production costs are 48,0 US $/t FeCr higher in the open furnace smelting.
- Electrode paste	25 kg	0,32	8,0	11 kg	0,32	3,5	
- Labour	35 operators		11,2	30 operators		9,6	
- Maintenance	-	-	17,3	-	-	20,0	
- Casting	(metal moulds)		5,1	(granul. slag)		0,0	When 50000 t FeCr/a is produced the annual extra cost is 2,4 mil. US $.
- Heating of ladles	(light oil)		4,5	(furnace gas)		0,0	
TOTAL			384,5			336,5	
	(Costs in US dollars)			(Costs in US dollars)			
Relative investment costs							The relative inv. costs are 30 % higher in the closed furnace smelting, when ore fines or concentrates are used. Gas cleaning systems are 200 % higher in the open furnace smelting
Coke drying and pelletizing of the concentrate			0			30	
Smelting:							
- gas cleaning			15			5	
- other equipments			85			95	
TOTAL			100			130	

UNITED NATIONS

ECONOMIC AND SOCIAL COUNCIL

RESTRICTED

ENV/WP.2/5/Add.10
3 July 1981

ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste Technology and Re-utilization and Recycling of Wastes

COMPENDIUM ON LOW-AND NON-WASTE TECHNOLOGY

Monograph

THE COMPARISON BETWEEN CONVENTIONAL AND LOW-WASTE NITRIC ACID PRODUCING TECHNOLOGIES

Transmitted by the Government of Hungary

1. Identification of industry

Manufacture of fertilizers. ISIC [1] code : 3512

2. Basic characteristics of production processes

The raw material of numerous nitrogen fertilizers is nitric acid which is currently produced with the help of the catalytic oxidation of ammonia. The basic processes of this technique are :

The raw material, ammonia gas, is diluted to a certain extent with air then oxidized at high temperature on platinum gauze which catalyzes the desired reaction.

The possible reactions of ammonia with oxygen are :

$$4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O + Q_1 \qquad (1)$$

$$4\ NH_3 + 4\ O_2 = 2\ N_2O + 6\ H_2O + Q_2 \qquad (2)$$

$$4\ NH_3 + 3\ O_2 + 2\ N_2 + 6\ H_2O + Q_3 \qquad (3)$$

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex).

Using platinum catalyst, because reaction (1) is almost complete, reactions (2) and (3) are only side reactions having minor importance. All the above reactions are exothermic, the temperature of the gas mixture leaving the reactor is between 1,070 and 1,200 Kelvin. The cooling of this hot gas is a stagewise process which is accompanied by the utilization of heat (steam production). In the cooling of the gas mixture a range of 300 to 320 K, the oxidation of nitric oxide (NO) takes place due to the presence of excess oxygen :

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2 + Q_4 \qquad (4)$$

This latter reaction is also exothermic, the removal of this heat can be accompanied by its utilization.

For the production of nitric acid, the nitrogen dioxide (NO_2) is absorbed in water or in dilute nitric acid solution :

$$3\,NO_2 + H_2O \rightleftharpoons 2\,HNO_3 + NO + Q_5 \qquad (5)$$

For the absorption of nitric oxides, counter-current absorption towers are used which are connected in series. The further oxidation of nitric oxide released during the absorption of nitrogen dioxide (see equation 5) also takes place in the absorption tower. Cooling water is used for the removal of the absorption heat. These oxidation and absorption processes are based on equilibrium reactions. They are always incomplete, so that the tail gas contains NO and NO_2 (designated as NO_x) causing marked losses in the production of the plant and pollution of the atmosphere. The other polluting agent is the waste water of the plant which contains nitric acid.

Today, for the enhanced absorption and utilization of nitrogen dioxide, absorbers are used which operate on elevated pressure. Moreover, a turbine is applied for the utilization of the pressure energy of the tail gas. In this case it is advantageous from the point of view of energy recovery to superheat the tail gas, but this causes heat pollution, which cannot be neglected.

3. Name of conventional processing technology

Modified SBA Process.

4. Description of conventional processing technology

For the production of nitric acid, the processes operating on atmospheric pressure have been generally substituted since the Second World War by the so-called combined processes. Numerous processes have been elaborated; their common characteristics are that the oxidation of the ammonia proceeds on atmospheric pressure and the oxidation of NO, and moreover the absorption of NO_2, is carried out at elevated pressure. One of these characteristic technologies is the SBA process which unites advantageously the significant points of the combined pressure processes. This process was further evaluated in Hungary and realized by the Pét Nitrogen Works. The process is discussed below.

4.1 Description of the unit operations/unit processes used in the production process

(a) Ammonia oxidation

The ammonia gas enters the plant through a pipeline with 1.1 atm pressure, the gas is filtred and mixed with filtred air blown by a fan. The mixed gas which contains 11.5 per cent v/v ammonia is filtred again and then led into the ammonia burner units. The units are equipped with Pt/Rh catalyst gauzes, three in each unit. Here the ammonia oxidizes at 1,110 to 1,130 K, at atmospheric pressure. The hot gases pass through a platinum recovery layer of CaO grains (OSW-system) and a "La Mont" heat recovery boiler where their temperature drops to between 440 and 460 K. The boiler produces steam with 36 atm pressure and 630 to 640 K temperature.

(b) The compression of gases

The gas leaving the La Mont boiler is cooled further with a water cooled heat exchanger to 305-320 K and compressed to 3.0 - 3.5 atm pressure by a turbo compressor. The compressor is driven by an electric motor and by an off-gas turbine. The temperature of the different stages of the turbo compressor is regulated by the variable amount of nitric acid solution injected into the turbine.

(c) The oxidation of nitric oxide

The gas leaving the compressor is cooled in a heat exchanger. The off-gas and the produced acid are used as a cooling medium. The cooled gas (350-370 K) enters into the two heat exchangers equipped with tube boundles and connected in series. These heat exchangers act as oxidizers. Here the gas cools to 310-330 K. Meanwhile the oxidation of nitric oxide to nitrogen dioxide takes place. Due to the condensation of water vapour, nitric acid forms which is led into the absorption system together with the condensed acid of the water-cooled heat exchanger mentioned above in (b).

(d) The absorption of nitrogen dioxide

The counter-current absorption system consists of eight absorber towers filled with Raschig rings. Four-four towers are connected in series. Into the last towers, water is fed which flows counter to the gas through the towers, due to gravity. From the first towers of the series, the acid produced leaves the system having a concentration of 50 to 52 per cent w/w. For the removal of the absorption heat, each absorber is equipped with a cooler and pumps for the recycling of the absorbent.

The acid produced which leaves the first towers is heated to 330 to 350 K with the hot gas produced by the ammonia burners, and the hot acid is pumped into the bleaching tower. Here the hot acid stream is blown through with fresh air for the removal of the physically absorbed nitrogen dioxide. The acid produced is stored in tanks. The air led through the bleaching tower contains nitrogen dioxide. This gas is recycled into the gas stream entering the turbo compressor. The oxygen content of this air stream covers the excess oxygen demand of the absorption process (see point 2).

(e) Energy recovery

The off-gas of the last absorbers contains 3.0 to 3.2 per cent v/v oxygen and 0.2 to 0.6 per cent v/v NO_x. This gas is heated in heat exchangers to 370 to 390 K and then led into the off-gas turbine. This turbine has a common shaft with the turbo compressor; it reduces the pressure of the gas : meanwhile the temperature of the gas sinks to from 340 to 350 K. This system recovers 30 per cent of the energy needed by the turbo compressor. The gas leaves the plant through a 60m stack.

(f) Additional equipment

The La Mont type heat recovery boiler has forced cycling. Its feed water consists of desalted and condensed water. Before using this water, it is degased by injection of steam. For regulating the salt content of the water, 10 per cent of the boiler water content is ejected periodically.

In the case of failures or shut down, the acid in the equipment can be drained into an underground tank. This acid can be reused if the plant starts again. Acid from leaks, or dripping valves, etc., together with the wash water is collected in a waste water canal and later pumped to a neutralizer. In a working unit, 12 pumps are in operation as, due to the leaking stuffing boxes, acid losses are unavoidable.

4.2 Specification of materials and energy requirements per ton of output

The following data are related to 1 t HNO_3 produced (the capacity of the plant is 10 t/hr HNO_3).

ammonia	297 kg/t
platinum	0.060 g/t (without recovery)
	0.015 g/t (with recovery)
feed wqter of boilers	1.2 m^3/t
recycled cooling water	145 m^3/t t = 7K
electric energy	260 kWh/t
steam (p = 3 atm)	0.2 t/t

by-products :

steam (p = 36 atm)
(t = 630° K/1.2 t/t)

4.3 Specification of the form and amount of airborne, waterborne, and solid wastes generated in the production process

The data below are related to 1 t HNO_3 produced

(a) Tail gas (air pollutant)

amount		1,950 Nm^3/t
temperature		350 K
composition	NO_x	0.3 per cent v/v
	O_2	3.5 per cent v/v
	H_2O	3.9 per cent v/v
	N_2	the rest

The off-gas leaves the absorption system and after the energy recovery stage it is vented through a 60 metre tall stack into the atmosphere.

(b) Acid waste water (water pollutant)

mean amount		0.02 - 0.06 m^3/t
HNO_3 content	maximum	5g/litre
	mean	0.10 - 0.5 g/litre

The sources of the waste water can be found dispersed throughout the plant, but come primarily from the absorption system. The cause is mainly the leaking stuffing boxes of the pumps.

(c) Salt containing waste water (water pollutant)

mean amount	0.12 m^3/t
concentration	1 g/litre NaCl or equivalent amount of sulphate, chloride or phosphate salts

(d) Solid wastes
None.

(e) Waste heat
The tail gas, specified in (a) causes heat waste.

4.4 Specification of the emission/effluent/solid waste standards applicable in Hungary

(a) Gas emission

The tolerated concentrations and measures are specified in Hungary by a departmental order (19/1974/XII.27./EVM), in which the following immission concentrations are listed regarding the NO_x gases :

For extremely protected areas	In max. = 0.05 mg/m^3 NO_x
For protected areas	In max. = 0.15 mg/m^3 NO_x
Other areas	In max. = 0.5 mg/m^3 NO_x
for Pétfürdo/Varpalota (the site of the plant)	In max. = 0.75 mg/m^3 NO_x

The expected values of immission can be calculated knowing the height of the stack and the actual capacity of the plant. If the responsible authority monitors a concentration higher than that listed above, the plant has to pay a fine.

(b) Water pollution

The concentration of acidic waste effluents is regulated by law (28/1978 MT). The allowed maximum concentrations - valid for acid producing plants - are :

salt	max.	2 000 mg/litre
oil	max.	10 mg/litre
ammonium-nitrogen	max.	30 mg/litre
pH		5-9

If the concentration of pollutants in the effluent waste water is higher than the given values, the plant is fined in accordance with the concentration and amount of the effluent.

(c) The standard dealing with solid wastes is under elaboration.

4.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

The air pollution produced by the described conventional processing technology is higher than that allowed by the standard. For lowering the emission, two possibilities can be taken into account :

(a) Catalytic off-gas purification

From the point of view of economy, it is important to continue the use of the installed equipment, although the original technology may be modified. Therefore, it seems to use ammonia as the reducing agent for the reduction of NO and NO_2 which are in the off-gas. This technology was elaborated by GIAP, and it is offered by Neftekhimprom Export in Moscow (USSR). The method is suitable for the reduction of NO_x concentration to 0.01 - 0.02 per cent v/v; the ammonia consumption in this case is about 2 kg/t nitric acid.

The above-mentioned method is elaborated on a commercial plant scale and is used by several plants in the Soviet Union. Further details about the method can be obtained from Neftekhimprom Export.

(b) Off-gas cleaning

A molecular sieve adsorption method for nitrogen oxides is elaborated on a pilot plant scale in Hungary. The advantage of this method is that the adsorbed nitrogen dioxide can be recycled in the gas stream processed in the absorption system. Further details of this method are at present unavailable.

4.6 Specification of the airborne, waterborne and solid wastes discharges into the environment

The above conventional processing technology does not apply purifying processes, therefore the specification of the wastes is the same as given under point 4.3.

4.7 Cost related data of the conventional production technology

The authors are of the opinion that the investment and operational costs of technologies realized in Hungary cannot be valued by specialists working in other countries; these data can be easily misunderstood. Therefore for the present purposes, it is recommended that material and energy requirements be given in relation to unit output rather than a selected monetary unit. For specialists in industry and economists, the values of the requirements mentioned may provide a basis for valuation and qualification.

Reference is made to the materials and energy requirements given under point 4.2, which may give a picture of the resource requirements. In addition to these factors, the manpower and capital requirements should also be taken into account.

Based on the data of two nitric acid producing units, each having a capacity of 250 t/day HNO_3, the number of operators per 8-hour shift is seven, plus the technical manager. This means 0.35 work-hour per 10 t HNO_3. The administrative and maintenance personnel are not mentioned as their number differs according to companies or countries.

For the evalution of investment cost of a nitric acid plant, the required amount of stainless steel can present a suitable basis. In the given case, the plant producing 250 t/day nitric needed 744 t of stainless steel. The latter means a specific stainless steel demand of 3.0 based on 1 t/day nitric acid production.

5. Name and state of development of low waste processing technology

The technology producing diluted nitric acid (60 per cent w/w) operates at 7.3 atm pressure. The technology is well developed and used on an industrial scale.

The technology was elaborated by GIAP (Scientific Planning and Research Institute on Nitrogen Industry and Synthetic Organic Products, Moscow, USSR). The name of the foreign trade company is : Neftkhimprom Export Moscow (USSR).

The present description summarized the significant and characteristic data of the above-mentioned low-waste technology which is operated by the Pét Nitrogen Works (Hungary). The plant consists of four production units : the total capacity is 120,000 t/year HNO_3 (15 t/hr). The plant started its production in 1975 and from this time it has run without major difficulties.

6. Description of low- and non-waste processing technology

6.1 Description of the unit operation/unit processes used in the production process

(a) The oxidation of ammonia

The air needed for the process is filtered (cloth filters) and compressed by a turbo compressor to 7.3 atm pressure. The main stream of the compressed air is led through a heat exchanger and into the ammonia-air mixing unit. The air-ammonia gas mixture containing 11 per cent v/v ammonia, heated to from 490 to 500 K, is filtered again and then enters into the ammonia burner at 7 atm pressure. In the burner the ammonia is oxidized to nitric oxide with the help of 12 platinum-palladium-rhodium catalyst gauzes; in this reaction the gas reaches 1,150 to 1,200 K. The hot gas passes through a waste heat boiler, where their heat content is used for the production of superheated steam. Leaving the boiler, the gas temperature is now 520 K.

(b) The oxidation of nitric oxide

The cooled gases are led into an oxidizer where a considerable amount of nitric oxide and oxygen from the excess air react, resulting in the formation of nitrogen dioxide. During this process, the gas temperature reaches 600 K. The gas is cooled in separated heat exchangers by air, off-gas and water to 320 K.

(c) The absorption of nitrogen dioxide

The cooled gas leaves the last heat exchanger with a pressure of 6.7 atm and enters into the absorption column just below its lowest plate. This absorber is equipped with 47 perforated plates having cooling coils above each plate for the removal of the absorption heat. The water, as absorbent, flows downward in counter current to the gas. The reactions taking place in the absorber are described under point 2.

The absorption of nitrogen dioxide begins in the last heat exchanger, which is cooled with water. Here the gas temperature sinks below its dew point and the condensed water reacts with nitrogen dioxide. Thus condensate, having a concentration of 50 per cent w/w nitric acid, leaves the heat exchanger at the bottom. It is led by gravity into the absorber over the perforated plate, on which the absorbent has the same nitric acid concentration.

The produced nitric acid has a concentration of 58 to 60 per cent w/w. It leaves the absorber and enters the bleaching tower where hot air (400 K) is blown through the acid stream for the elimination of its physically absorbed nitrogen dioxide content. The air, with a high nitrogen dioxide content, is united with the gas stream entering the absorber column. This amount of air supplies the excess oxygen needed for the oxidation of nitric oxide, which is produced during the absorption of nitrogen dioxide in water. The bleached acid which is produced flows into the storage tank. From here it is pumped to the fertilizer plant.

(d) The catalytic processing of the off-gas and the energy recovery

The off-gas leaving the absorber contains about 3 per cent v/v oxygen and 0.08 to 0.10 per cent v/v NO_x. This gas is treated for the removal of nitrogen oxides.

A catalytic treatment is used for the desoxidation of NO_x. For this purpose methane is applied, and the catalyst is palladium with aluminium oxide. The catalyst is unselective, so besides the NO_x, the oxygen of the off-gas is also consumed. Actually, this latter process is required for the removal of the nitrogen oxides.

The reactions taking place over the catalyst surface are listed below :

$$2\,CH_4 + O_2 = 2\,CO + 4\,H_2 + Q$$
$$2\,NO_2 + 4\,H_2 = N_2 + 4\,H_2O + Q$$
$$2\,NO + 2\,H_2 = N_2 + 2\,H_2O + Q$$
$$2\,CO + O_2 = 2\,CO_2 + Q$$
$$2\,H_2 + O_2 = 2\,H_2O + Q$$

The catalytic process is carried out as follows : The off-gas is heated in a heat exchanger to 380 or 400 K with the gas leaving the ammonia burner. Then the gas is heated further to 650 or 670 K with flue gas produced from burning methane in air. This latter has a temperature of from 1,300 to 1,700 K. A measured amount of methane is mixed with the preheated gas and this mixture is fed into the catalytic reactor where the above-mentioned reactions take place.

As the reactions are exothermic, the gas mixture reaches a temperature of 970 to 1,000 K. The gas leaves the reactor at 5.9 atm pressure.

For the return to normal pressure and recovery of heat energy of the cleaned gas, it is led into a turbine where it expands to atmospheric pressure and its temperature decreases to 680 K. The released energy of the expanding gas covers the energy demand of air compression as the turbine is connected to the air compressor. To this unit is also attached an electric motor for starting the compressor.

As previously described, the off-gas cleaning and the energy recovery is combined. Almost the total chemical energy of the natural gas used for the elimination of NO_x is recovered as mechanical energy in the turbine. This gas cleaning process is a part of the technology and it cannot be evaluated either energetically or apart from the whole process.

(e) The pretreatment of ammonia

The liquid ammonia which arrives at the plant at a pressure of 16 atm is led to a separate pretreatment unit. Here it is evaporated to 12 atm pressure with the help of steam, and the ammonia gas is washed with liquid ammonia in a still equipped with bubble cap trays for the elimination of impurities. The clean ammonia gas is preheated in a heat exchanger to 380 K with steam. This ammonia gas is used as raw material in the ammonia burning units.

It should be mentioned that in the near future only clean, gaseous ammonia will be processed which will result in the saving of steam and energy.

(f) The pretreatment of feed-water and steam production

The heat exchangers and heat economizers have a major role in the heat balance of nitric acid production. For the feed-water supply, a pretreatment unit is used which consists of feed-water preheaters, thermic degasers and pumps.

All production units are equipped with two heat economizer boilers. One is used for the cooling of hot gases leaving the ammonia burners and one for the cooling of the cleaned off-gas which leaves the turbine. The former boiler produces more, about 75 per cent, of the total produced steam. Both boilers produce superheated steam at 510 K and 16 atm. The boilers are connected to a common steam line and completely meet the steam demand of the nitric acid plant. The surplus steam is used for evaporation purposes in the fertilizer plant.

(g) The treatment of waste acid

The waste acids originating from the emptying of pipelines, tanks, etc., are led to a separate, underground storage tank from where plunger pumps transfer the acid to tanks containing the produced nitric acid.

The waste acids originating from seepage, leaking, and the acid wash water are also collected in an underground basin. If the concentration of acid solution in the basin is higher than 5 g/litre HNO_3, it is filtered and mixed with the produced nitric acid. If its concentration is between 5 and 0.5 g/litre, it is used for neutralization of ammonia-containing waste water produced in the ammonia and fertilizer plants; if it is less than 0.5 g/litre, it is passed from the plant site without any pretreatment.

(h) Platinum recovery

Filters are used for the recovery of platinum metal particles from the gas stream leaving the ammonia burner units. These filters remove a considerable part of the platinum content of the gas.

6.2 Specifications of materials and energy requirements per ton of output

The following data are related to 1 + HNO_3 produced (the unit produces 15 t/hr HNO_3)

ammonia	0.293 t/t
platinum	0.160 g/t (together with platinum recovery)

	desalted water	2.3 m^3/t
	condensed water	0.4 m^3/t (used for absorption)
	recycled cooling water	160 m^3/t $\Delta t = 7$ K
	natural gas	130 Nm^3/t
	palladium (100 % Pd)	0.017 g/t (for off-gas treatment)
	electric energy	20 kW/t
by-products :		
	steam (p = 15 atm, t = 500 K)	1.5 t/t
	condensed water	0.3 m^3/t

6.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

The data below are based on 1 ton nitric acid produced

(a) Off-gas (air pollutant) (stack gas)

amount		4,1200 Nm^3/t
temperature		450 K
composition	NO_x	0.005 % v/v
	CO	0.1% v/v
	CO_2	2.5% v/v
	O_2	0.9% v/v
	CH_4	0.2% v/v
	H_2O	5.8% v/v
	N_2	the rest

The off-gas leaves the plant through a 100 metre stack into the atmosphere.

(b) Acid waste water (water pollutant)

amount	0.005 - 0.01 m^3/t
max. HNO_3 content	5 g/litre
mean HNO_3 content	0.1 - 0.5 g/litre

The origin of these nitric acid-containing waste waters is the seeping and leaking of pipes, valves, tanks, etc., and the wash water of equipment. This water, depending on its nitric acid concentration, leaves the nitric acid plant (see point 6.1).

(c) Waste water containing salt

This waste water is produced by the periodic blowdown of the heat economizer boilers. The blowdown is cooled and drained.

amount	0.01 m^3/t
concentration	1 g/litre NaCl or equivalent amount of sulphate, chloride or phosphate salts.

(d) Solid wastes

None.

(e) Waste heat

The stack gas specified in (a) above carries considerable heat. Therefore it causes energy loss. At present there is no economical solution for the recovery of this heat.

6.4 Specification of the emission/effluent/solid waste standards applicable in Hungary

The standards in force in Hungary were described under point 4.4.

6.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

For the reduction of pollution, the purfiication of the stack gas is necessary. However, since this is an integral part of the technology (see 6.1 (d)) and as the efficiency of the gas cleaning is high, further purification processes are unnecessary.

The amount of effluent is negligible in the case of the technology discussed. There is no need for pumps to recycle acid (the gas coolers are suitable planted, absorption heat is removed by cooling coils mounted above the perforated plates of the absorption column; therefore, additional acid cooling and recycling is not needed compared with the classical absorption columns filled with Raschig rings). It is well known that the main sources of the effluent acid waste waters are the leaking and dripping stuffing boxes of the pumps. In lessening the number of pumps, the sources are restricted.

As desalted water is used as feed water of the boilers, there is no build-up of salt deposits in them during steam production.

6.6 Specification of the airborne, waterborne and solid waste discharges into the environment

There are no additional cleaning processes as discussed under point 6.1 in the description of the recommended low-waste technology. Therefore, the specification of the wastes is the same as described under point 6.3.

6.7 Cost-related data intended to permit comparison of low- and non-waste technology with conventional technology

As described under point 4.7, the costs of the low-waste technology of nitric acid production can be given by the prices of the amounts of raw materials and energy used. These should be completed by adding the labour costs.

In the plant discussed, for the units producing 360 t/day nitric acid, eight operators per shift are needed. Therefore, the direct labour demand is 0.14 hr/t nitric acid. Referring to point 4.7, the invested amount of stainless steel, based on 1 t/day nitric acid production is 1.5 t.

The specific invested amount of platinum gauze is 78 g platinum per 1 ton of nitric acid per day.

7. Schematic comparison between the conventional and low-waste technology

7.1 Materials and energy requirements

The data are based on 1 ton produced nitric acid

	A conventional technology	B low-waste technology	A minus B
ammonia kg	297	293	4
platinum g	0.06	0.16	-0.10
processed, desalted water, m^3	1.8	2.7	-0.9
energy Mcal	330	5	325

The net energy demand was taken into account (e.g. from the total energy demand, the produced energy - steam, etc. - was subtracted, and for the comparison made the calory unit was selected). In the calculations, the following energy sources were used :

natural gas	8 500 kcal/m^3
steam	1 000 kcal/kg
electricity	4 000 kcal/kWh
cooling water	2 000 kcal/m^3

Sections 4.2 and 6.2 deal with other items.

It is evident from the data listed above that the proposed low-waste technology has major advantages from the point of view of energy consumed. Its obvious drawback lies in the higher consumption of platinum catalyst.

7.2 Generation of airborne, waterborne and solid wastes

The data below are based on 1 ton produced nitric acid.

		A conventional technology	B low-waste technology	A minus B
Air Pollution				
stack gas	Nm^3	1,950	4,120	-2,170
in the stack gas				
NO_x	Nm^3	5.9	0.2	5.7
CO	Nm^3	-	4.1	-4.1
CO_2	Nm^3	-	103.0	-103
Water pollution				
Acid waste water total	m^3	0.04	0.008	0.032
HNO_3 in the acid water	g	12	2.4	9.6

		A conventional technology	B low-waste technology	A minus B
Water pollution (contd.)				
salt containing waste water (from boilers)	m^3	0.12	0.01	0.11
salt content (NaCl)	g	120	10	110
Solid waste	kg	-	-	-
Waste hear				
Temperature of stack gas	K	350	450	-100
heat content (referred to 20 °C)	Mcal	35.6	207.0	-171.4

In comparing the above data, it is evident that the proposed low-waste technology produces a stack gas having very low NO_x concentration, although its carbon monoxide content is an additional polluting agent. Fortunately, the CO concentration is considerably lower than the limit of the standard. Regarding liquid effluents, the advantages of the proposed technology are evident. From the point of view of waste heat, the proposed technology is under a heavy handicap. Undoubtedly, in the furure further tehhnical developments will lessen this disadvantage and will improve the - otherwise favourable - heat balance of the process.

7.3 Pollution control measures needed for compliance with existing standards

There are no known processes in our hands for the further treatment of the above-mentioned wastes.

7.4 Discharges of airborne, waterborne and solid wastes

As mentioned under point 7.3, for lack of more up-to-date waste treatment processes, the wastes of the process discussed are the same as described under point 7.2.

7.5 Investment requirements and unit production costs

Reference is made to point 4.7, where the specific material and energy consumption has to be compared (as it was done under point 7.1) and the following specific data have to be taken into account :

Reproduced from best available copy.

	A conventional technology	B low-waste technology	A minus B
direct need of work hours/t HNO_3	0.35	0.14	0.21
platinum gauze needed per 1 ton nitric acid per day (g)	134	78	56
stainless steel needed per 1 ton nitric acid per day (t)	3.0	1.5	1.5

The data in the above table show clearly the advantages of the proposed technology regarding investment and operating costs.

7.6 Other significant differences between the conventional and the low-waste technologies

The conventional technology produces nitric acids with 50 to 52 per cent w/w concentration while the product of the proposed technology is 58 to 60 per cent w/w. It is evident that more concentrated acids are advantageous.

8. Identification of needs for further research and development with regard to the low- and non-waste technology

Under point 6.1 (c) it was mentioned that the plant will use in the future gaseous instead of liquid ammonia. This alteration will improve the energy balance of the production, but it will have no effect on the pollution generated by the plant.

Also, it was mentioned under point 7.2 that reduction of the stack gas temperature with the help of a suitably arranged heat exchanger will improve the energy balance of the technology and will lessen the heat pollution of the environment.

Unfortunately, we are not informed about research work carried out in this field.

9. Reporting organization

Pét Nitrogen Works
Varpalota, P.O. Box 50,
H-8105

Veszprém University of
Chemical Engineering
Veszprém, P.O. Box 28,
H-8201

National Authority for Environment Protection
and Nature Conservation,
Budapest, XII
Költo -u. 21
H-1531

Reproduced from best available copy.

10. Date of report

September 1979.

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

RESTRICTED
ENV/WP.2.5.Add.11
6 July 1981
ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

PRODUCTION OF NPK FERTILIZERS THROUGH THE NITRO-PHOSPHATE (OR ODDA) PROCESS WITH CONVERSION OF CALCIUM NITRATE AND RE-CIRCULATION OF NITROGEN AND PHOSPHOROUS EFFLUENTS

1. Identification of industry

Manufacture of fertilizers. ISIC [1] code : 3512

2. Basic characteristics of production process

The industry is characterized by a variety of processes leading to the same type of products, where the choice of process is often dependent on local circumstances. A rough distinction may be made between the processes utilizing supphuric acid as an intermediate material to dissolve phosphoric rock and those processes which utilize nitric acid for this purpose.

3. Name of conventional processing technology

Manufacture of complex fertilizers on the basis of wet process phosphoric acid.

4. Description of conventional processing technology

There are a number of processes for the production of complex fertilizers. The two principal inputs in a fertilizer complex are sulphuric acid and wet-process phosphoric acid. The sulphuric acid unit is essential to the phosphoric acid plant not only for the sulphuric acid raw material, but also for the production of steam for operating vacuum and evaporation equipment. Phosphoric acid is the basic raw material for straight phosphate fertilizers and ammonium phosphates.

The nitrogen component in the complex may be provided either as essentially ammonical nitrogen in the form of ammonia and urea or as partly ammonical and partly nitrate nitrogen in the form of ammonia and nitric acid.

---

[1] International Standard Classification of All Economic Activities (ENV/WP.2/5/Annex).

GE.81-42157

As a by-product from production of phosphoric acid, large quantities of gypsum have to be disposed of or converted into useful products, which has proved to be both expensive and an environmental problem. Flow sheets for sulphuric acid, phosphoric acid and monoammonium phosphate processes are given as examples in Figures 1 to 4 with a schematic presentation of gypsum disposal problems.

The granulation process taken as example in this paper uses phosphoric acid and nitric acid as raw materials. A flow diagram is given in Figure 5. The acids are neutralized with ammonia, granulated, dried, screened and cooled. Effluents are treated in cyclones and scrubbers.

5. Name and state of development of low- and non-waste processing technology

The name of the low- and non-waste technology is the Norsk Hydro nitro-phosphate (Odda) process.

The Odda nitrophosphate process has been in existence in Norway since about 1930. Several modifications have been introduced by Norsk Hydro, and the process today offers the following advantages :

- No need for sulphur as a raw material.
- CO_2 that otherwise would have been wasted from the NH_3 plant is used for conversion of the calcium nitrate by-product.
- More than 99 per cent of the P_2O_5 contained in the phosphate rock ends up in the NPK product compared to 95 per cent by conventional technology.
- Nitric acid attack on phosphate rock gives a low fluorine emission that is easily cleaned up.
- NO_x effluents are effectively controlled by urea addition.
- The process avoids the 4 tons of waste gypsum produced per ton P_2O_5 by the conventional wet process phosphoric acid technology.
- The energy requirements are low.
- The production costs are favourable compared to those of conventional technologies.

Presently, the nitrophosphate processes accounts for 12 per cent of the total complex fertilizer capacity in Western Europe and 25 per cent in Eastern Europe.

6. Status of the Norsk Hydro nitrophosphate process

Norsk Hydro started its first NP/NPK plant in Norway in 1936. The company now has three plants in operation, one at Glomfjord in northern Norway with a capacity of 1400 t/d, one at Porsgrunn with a capacity of 1100 t/d, and the newest one, also at Porsgrunn, with a capacity of 2500 t/d. The plant at Glomfjord produces granulated NPK using pugmills, whereas the two plants at Porsgrunn both have prill towers.

The following plants are in operation in other countries :

Hungary has one plant with a capacity of 2200 tons of NPK per day. The water solubility is 80 to 85 per cent. The calcium nitrate is converted to ammonium nitrate solution. The amount of ammonium nitrate being used as a nitrogen source in the NPK plant is dependent on formulations of the product. The excess of ammonium nitrate will be processed into ammonium nitrate limestone fertilizer in an adjacent plant. In this plant the calcium nitrate from the filters also can be processed into nitrate of lime fertilizer. Romania has four NP and NPK plants. The capacity of each of the plants is about 2700 metric tons per day. Water solubility is 80 to 85 per cent. Conversion plants for converting calcium nitrate into ammonium nitrate solution are included.

In addition, five plants are under construction in the USSR, each with a capacity of about 1850 t/day of 16.5-16.5-16.5. Greater daily production capacity will be achieved for other product formulas. Conversion plants for calcium nitrate and liquid recycle systems are included. One plant is under construction in the People's Republic of China with a design capacity of 3000 t/d of NP fertilizer. A conversion plant and an effluent recycle system are included. A reference list is enclosed in Tables 1 and 2. The contract with China will bring the total number of plants based on Norsk Hydro's licence to 12 with a total production capacity of about 8.5 million metric tons per year.

7. Description of low- and non-waste processing technology

The Norsk Hydro NPK-process consists of the following main process steps : (Fig.6)

- Acidulation of phosphate rock.
- Crystallization of calcium nitrate tetrahydrate.
- Filtering of the calcium nitrate crystals.
- Neutralization of the mother liquor and addition of ammonium nitrate.
- Evaporation of the neutralized liquor.
- Mixing of the melt with recycled fines and, if required, with potassium salts and micro nutrients.
- Prilling of the mixture in an air-cooled prill tower.
- Cooling, screening and coating of the final product.

The calcium nitrate which is filtered off can either be processed into nitrate of lime fertilizer or it may be converted to ammonium nitrate and calcium carbonate.

Acidulation

The acidulation in practice means that the rock phosphate with particle size less than 1 mm is dissolved in nitric acid. The nitric acid should not be of less strength than 58 to 60 per cent. The heat evolved raises the temperature to from 50 to 70 °C, depending upon the rock phosphate composition.

The acidulation takes place in two consecutive stirred tank reactors. An excess of nitric acid is used to prevent the precipitation of monocalcium phosphate in the ensuing stage. If required, a small amount of defoamer is also fed into the digestion tank.

Some of the hydrogen fluoride produced reacts with silica in the rock to form fluosilic acid. A small amount of the rock fluorine escapes from the digestors as SiF_4 and HF, which, together with oxides of nitrogen formed in the reaction, are removed by wet scrubbing in the fume scrubbing section. The formation of nitrogen oxides can be reduced by the addition of urea.

Crystallization

Crystallization of calcium nitrate tetrahydrate, $Ca\,(NO_3)_2\ 4H_2O$, by deep-cooling is one of the key features of the Norsk Hydro NPK process.

The crystallization process is carried out semi-batchwise in a series of stirred vessels equipped with cooling coils and cooled by 20 per cent aqueous ammonia solution. A significant part of the cooling load required in the crystallization is derived through evaporation of the ammonia for the neutralization.

The operation of the crystallizers is arranged in such a manner as to produce an overall effect of continuous operation. Coolant from the refrigeration section enters the coldest crystallizer in the most advanced stage of crystallization and then flows successively through each crystallizer to the warmest crystallizer containing a fresh charge of acidulation liquor.

When the coldest crystallizer has reached the temperature required, the mother liquor and crystals are discharged to a stirred vessel, the content of which is fed to the calcium nitrate filters at a steady rate. Warm acidulation liquor enters the crystallizer which has just discharged its load and regenerates the cooling surface by melting the adhering calcium nitrate tetrahydrate crystals. The whole operation of crystallization can be completely automated.

The solubility of $Ca(NO_3)_2 4H_2O$ in the acidulation liquor decreases rapidly with decreasing temperature. The solubility is also influenced by the concentration and excess of nitric acid in the liquor.

The crystallization of $Ca(NO_3)_2 4H_2O$ starts at about 25 °C. In the deep-cooling process the solution is cooled down to from 0° to -5 °C. This is at present as far as it seems economical to go, taking into consideration the time required and cooling costs. This results in a Ca/P ratio of approximately 0.35 and a water solubility in the end product of 80 to 85 per cent.

Filtration

The suspension of mother liquor and crystals is filtered on rotating tandem filters designed and constructed by Norsk Hydro. These filters have proved to be very reliable and can be operated for months without any maintenance. Previously, other techniques of crystal removal had been tried, but the filtering method employed today surpasses other known methods. The crystals are washed with nitric acid and water. The wash acid is returned to the acidulation.

Neutralization and evaporation

The neutralization takes place in two consecutive stirred tank reactors. Gaseous ammonia is added to the mother liquor from the filtration under strict pH control.

During the neutralization, practically all the calcium and fluorine in the mother liquor are precipitated as $CaHPO_4$ and CaF_2. The liquid phase is a solution of ammonium phosphates and ammonium nitrate.

If no ammonium nitrate is added to the mother liquor, the N/P_2O_5- ratio of the neutralized liquor is about 0.7 to 0.9, depending on the Ca/P-ratio in the liquor, and the amount of excess nitric acid present. The N/P_2O_5-ratio can be adjusted upwards by addition of ammonium nitrate to the mother liquor. Thus, the N/P_2O_5-ratio in the process can be varied from about 0.7 and up. By recycling the total amount of ammonium nitrate from the conversion plant (described below) an end product with N/P_2O_5-ratio is required, ammonium nitrate from another source must be added. Before its addition to the mother liquor, the ammonium nitrate is normally concentrated to from 80 to 90 per cent.

Neutralized and N/P_2O_5 adjusted liquor from the neutralization is pumped to the evaporation stage. During evaporation, the water content is reduced to 0.5 per cent in the evaporators of Norsk Hydro's own design. The evaporation takes place in two stages under vacuum. The evaporators are designed to prevent precipitation of ammonium phosphate and scaling of the heat transfer surfaces. Scrubbing units take out fluorine and ammonia in the vapours released during the evaporation. By careful design and recycling of the scrubbing liquid, the effluent from the plant can be minimized.

Mixing and prilling

The mixing and prilling is another key part of the Norsk Hydro NPK process. The equipment used here is of the company's own design, based upon years of experience.

The almost water-free NP-melt from the evaporators can be prilled as such, making for instance 23-23-0, or it can be mixed with a potassium salt and other additives such as $MgSO_4$ and Borax before prilling.

It is in the nature of the prilling process that the cost of the prilling tower is nearly independent of the plant capacity. Thus, the advantages of the prilling process increase with the size of the plant. However, in order to give an idea of the order of magnitude as to the size of the prill tower, a tower of diameter 25 m and with free falling height of the particles of 40m will be adequate for the production of more than 100 t/hr of product.

The product leaving at the bottom of the prill tower has a temperature of from 80 to 100 °C and has to be screened, cooled and conditioned before going into storage. The screens take out the oversized and undersized elements. Those oversized are crushed and screened again, whereas the undersized elements are returned to the mixer. The recycling rate of the fines is in the order of 5 to 10 per cent of the total production.

Conversion of calcium nitrate

The calcium nitrate by-product can either be used in the production of nitrate of lime or be converted into ammonium nitrate and calcium carbonate.

The nitrate of lime fertilizer contains 15.5 per cent nitrogen, and is, for special agronomic purposes, an excellent product. It is hygroscopic, but when prilled and conditioned, as done by Norsk Hydro, it attains excellent storage properties and may even be shipped in bulk.

However, if the conversion is favoured, this is done in a conversion plant as shown in Figure 7. Ammonia and carbon dioxide are absorbed in a solution of ammonium nitrate forming ammonium carbonate. This solution and the calcium nitrate melt are fed to a reactor tank where conversion to ammonium nitrate and calcium carbonate takes place. In a correction tank additional ammonia and carbon dioxide (solution) can be introduced if necessary.

The suspension is filtered on a rotating filter, and the filter cake of calcium carbonate is washed with hot water. A final clarification of the ammonium nitrate solution can be carried out in an additional polishing filter-unit.

Part of the ammonium nitrate solution produced is recycled to the absorption unit. The ammonium nitrate solution contains about 40 per cent water, and the amount that leaves as a product from the conversion plant may be further evaporated.

8. Schematic comparison between the conventional and the low- and non-waste technologies

8.1 Materials and energy requirements

The economy of nitrophosphates versus sulphur-based complex fertilizers as presented in this paper are summarized for the sulphuric, phosphoric and nitric acid plants needed, and corrected for the AN by-product from the nitrophosphate plant. These calculations are given in Tables 3 and 4. Based on sulphur, phosphate rock, ammonia, potassium chloride and carbon dioxide as raw materials, the consumption figures for the complex is given in the table below : All figures are per metric ton P_2O_5 in the product.

Input element	Nitro-phosphate NPK	Sulphur based NPK	Saved by nitrophosphates
Raw materials			
Sulphur (tons)	0	0.97	0.97
Phosphate rock 33% P_2O_5	3.06	3.15	0.09
CO_2, tons	1.06	0	-1.06
NH_3, tons	1.23	1.28	0.05
KCl, tons	1.64	1.67	0.03
Utilities			
Steam, tons	5.59	6.69	1.10
Water, tons	382.6	580.8	198
Fuel oil, tons	0.03	0.065	0.035
Electricity, kW	395.2	392. 1	-3.1

The carbon dioxide needed for the conversion of calcium nitrate is usually available from the ammonia plant at no cost. Further, the nitro-phosphate process offers a more efficient use of raw materials and also a slightly advantageous use of utilities.

8.2 Pollution control measures needed for compliance with existing standards

Water pollution control

In the beginning of 1974 the Norwegian authorities issued a new regulation for allowable P_2O_5 -outlet from two complex fertilizer plants at Poragrunn Works.

The limit was specified to a total of 46 kg P_2O_5 per day and a maximum outlet concentration of 2.3 mg P_2O_5/litre in the total effluent stream from each plant. The two plants have a total capacity of approximately 3,500 tons of NPK-fertilizer per day.

The nitrogen limit in the effluent water was not specified to the same extent as for P_2O_5. The authorities merely asked for a survey of possible reduction, pertaining to the Poragrunn Works as such, down to 50 per cent of the existing level. No definite time limit was given as to realization of such a reduction.

Basic process principles

From the beginning the principle prevailed of establishing a recycle process for the treatment of liquid effluents. The reason was to recover not only phosphorous, but also, at least partly, the nitrogen.

The pond collection system was not considered appropriate in this case. A pond, apart from having a high investment cost due to needs for ground protection, would merely act as a collector and would ultimately need emptying and cleaning. This could cause rather long shut-downs of the fertilizer plant. Therefore, a process was worked out for a continuous and controlled treatment of the effluent streams with continuous recycle of residuals back to the NPK plant.

A survey was made in the NPK plant to record the amount and composition of all individual effluent streams. These streams do contain the same components, i.e. phosphorous, calcium, nitrogen and (partly) chlorine, and it should be logical to collect and treat them as one combined stream. However, due to the safety hazard of evaporating nitrate-containing liquids containing traces of chlorine or copper, chlorine polluted water must be kept in a separate system.

Consequently, a distinction must be made between :

- Cl-containing systems
- P-water systems

The water-balance of the enclosed system is maintained by using the P-water as regular, continuous wash water on the calcium-nitrate filters and as wash water to a system for removal of sand (acid insolubles) from the process liquor. By balancing the water entering by condensation, drainage and washing against this consumption, losses of P-water could be kept at a very low level.

Description of the system

The system is described in the flow sheet presented in Figure 8.

Cl-water from the dry section is collected in a sump and further pumped to the Cl-water tank while wash water from the mixing/prilling area goes directly to the tank.

A continuous pumping circuit is established for Cl-water to the consuming units with bleed-back to the tank.

The Cl-water is transferred to the P-water system according to the analysis of the Cl-content in the P-water and then is substituted by cleaned water from this same, P-water circuit.

P-water from the wet section enters into a sump, and a similar pumping circuit is established from the cleaned water tank.

For routine cleaning of NP-evaporators a collection tank has been installed. The contaminated water from this tank and from the P-water sump is sent to the P-water tank. By addition of NH_3, and $Ca(OH)_2$, precipitation of calcium phosphates and fluorides, etc., takes place.

By addition of a polyelectrolyte-type flocculating agent, an efficient sedimentation of the precipitate will occur.

The underflow from the sedimentation tank is pumped via a sludge tank to a centrifuge.

Solid material from the centrifuge is flushed back to the NPK-process while the liquid phase flows to the P-water tank.

To handle large fluctuations in the demand for wash water, another buffer tank was installed in this plant. The tank serves as a buffer both for the Cl-water system and the P-water system and can be emptied by drainage to the Cl-water sump.

The water balance in the system is, as already described, maintained by using cleaned water as continuous wash water on the calcium nitrate filters. To reduce dissolution of calcium nitrate crystals, this water is cooled before entering the filter.

Another water-consuming source would be washing of sand (acid insoluble particles) removed from the process liquor.

In addition, the P-water can be returned according to the extent of the NP-evaporator capacity.

Operating experience

The liquid recycle plant met the scheduled start-up date and has now been in regular operation for more than a year with very satisfactory results.

The regular operation of the NPK plant has been affected very little, both during start-up and later. Actually only five days of shut-off were needed in order to incorporate the unit into the existing plant. One additional shift operator has been allocated for the liquid recycle plant.

From the beginning **great** emphasis was placed on automatic process control and considerable instrument adaption was made, thus managing satisfactorily both an automatic Cl- and P_2O_5-analyzer.

As to P_2O_5-effluent, the results have been very satisfactory. The amount now varies from 25 to 45 per cent of the permitted amount, or from 7 to 12 kg P_2O_5/day for the No. 3 plant.

The nitrogen recovery has not been measured in detail - a rough estimate seems to indicate that at least 3 tons/day of nitrogen is recovered by this installation alone.

From this pioneer installation one can see today the possibility of several simplifications for future installations. Such installations, particularly in connection with the granulation technology, could be made with rather moderate investment cost.

Typically, a preliminary estimate for installed cost (exclusive all building costs) of a plant connected to a NPK plant with a capacity of 6 to 7 tons P_2O_5/hr would be approximately US$ 1 million.

Operating cost for the installation would be rather low, and negligible compared to the overall NPK plant.

Air pollution control

The extent of necessary cleaning equipment will vary from plant to plant as to variation in the limits of emissions. In this monograph we can merely point to the characteristic contaminants in air and vapour from the different sections of the plant and thus to possible principal abatement installations.

Emission from the wet section and from the NP-evaporation section

In this respect, the wet section can be further divided into the acid section, and the alkaline section.

From the acid section (comprising basically digestion, crystallization and calcium nitrate filtration), the main components to be treated would be fluorine, nitrous oxides and nitric acid vapour.

As is well known, the fluorine-release from nitric acid attack on phosphate rock is considerably lower than from sulphuric acid. In the nitrophosphate case this release could be around 0.5 to 1 per cent of fluorine in phosphate rock input. Thus, when the vent air has passed a simple scrubber, it is normally below the requirements on F-concentration in vent air.

The advantage of urea-addition to suppress formation of nitrous oxides are well known. It should be mentioned that the addition of urea in all fertilizer plants has continued with the best of results. Thus, we are now, by maintaining only a simple scrubbing installation, able to control the stack concentration at about 100 to 150 ppm NOx by keeping the proper surplus of urea in the digestion tanks.

The alkaline section (neutralization and conversion) has to be treated for ammonia emission. Ammonia is released together with water vapour from the neutralizers and the scrubbing may be carried out in different ways, such as by using nitric acid to make an ammonium nitrate solution or by condensation and absorption in water followed by stripping of the ammonia. Vapour from NP-evaporation does contain small amounts of fluorine in addition to ammonia.

The recovery may, in principle, be performed as for the neutralizers. However, due to the simultaneous release of fluorine, a fluorine scrubber has to be installed as the first step. The fluorine can in such a case be absorbed in the ammonium nitrate solution.

If a condensation/stripping method is used, it is recommended to maintain the fluorine scrubbers to eliminate scaling by SiO_2 in the condenser, as fluorine is partly evolved as SiF_4 during evaporation of NP-melt.

Emission from dry section

Contrary to the general experience from prilling of straight nitrogen fertilizers, there is very low dust formation in this prilling process for NP/NPK-fertilizers, the reason being that the prilling temperature of NP/NPK is well below the boiling point of the NP-melt due to addition of KCl and recycling. Thus, the typical fume formation does not contribute significantly to the emission in this case.

The amount of dust that adheres to the product surface and which can actually be sluffed off later at transfer points (or in storage or handling) is lower in a prilling operation than in granulation. Such dust is also very efficiently incorporated in the NP-melt in the prilling operation. Moreover, the round, smooth surface of the prills causes a lower level of abrasive dust.

The spinning basket type has the advantages of producing a relatively narrow size range for prills. A wider tower must be used compared to the stationary straw prilling device and this results in lower linear velocity and less particle entrainment from the tower.

Overall, these advantages mean that the air from the prill tower in this nitrophosphate process would not need to be treated as it has normally a dust content of about 5 mg/Nm^3.

Cooling is performed in a rotary drum ~~in~~ this plant, and only dry cyclones are needed for the cooling air to control dust emission at an acceptable level.

Vent air from other equipment in the dry section, i.e. screens, elevators, mill, etc., is combined with venting of equipment for return of off-size material to the NP-melt. A bag filter, located on top of the prill tower, is used for this purpose. The collected dust can then easily be returned to the NP-melt in the mixer.

The coating system in this plant has separate dust collection with a bag filter, and ventilation of the coating drum in incorporated into the system.

Emission from KCl-preparation section

Our prilling process utilizes commercially available KCl.

A certain scalping with subsequent crushing of oversize is, however, needed. Some heating and drying of the salt may also be needed.

The vent air from these operations is treated in bag filters and the collected dust is incorporated in the regular KCl-supply to the mixer.

8.3 Investment requirements and unit production costs

The various production routes will require different raw material, and present investment costs and production costs for sulphuric acid and nitric acid based upon European conditions have been established. The resulting sulphuric acid prices have then been used for establishing the phosphoric acid production cost, and this price has subsequently been used as a base for the sulphuric acid based process. As for ammonia, world market prices of 140 $/t product has been introduced, and phosphate rock of 72 BPL = 33% P_2O_5 has been priced at $35/t. The price of KCl will have little influence on the relative price, and the current price of $65/t KCl has been used.

The price of sulphur is a key factor in a comparison of this sort, as it is a cost factor which cannot be credited to the final product, because sulphur is used for production of sulphuric acid, but also discarded in the form of gypsum in the phosphoric acid production. Furthermore, the availability of sulphur (and consequently also the price) varies considerably between different areas. A market price of 75$/t sulphur has been chosen as a representative average.

The nitrophosphate process will also give a by-production of ammonium nitrate. This is credited in the way that a production cost price for ammonium nitrate on a similar basis to the other production cost prices has been established. Thus, the amount of by-product ammonium nitrate equivalent to 1 t P_2O_5, which is 3.40 t AN/t P_2O_5, can be credited for the production.

Capital costs have, in all calculations, been taken to be 20 per cent per year of the total investment costs, and yearly maintainenance has been taken as 5 per cent of the investment costs. Labour costs, however, have been established for each production unit individually, based upon 68$ man-day, and 5 shifts for each plant.

As to utilities, electricity prices of 35 mills/kWh ($0.035) have been used, steam at 15 $/ton, cooling water at 0.02 $/ton, fuel oil at 140$/ton and platinum for nitric acid plant at 10$/grm.

The nitrophosphate plant requires the availability of CO_2 from an external source. As long as this is available, it has been considered at no charge. Some 330 operating days per year have been assumed.

The comparison is summarized in the following table :

	Production cost per ton P_2O_5
Nitrophosphate with crystallization of calcium nitrate, conversion to ammonium nitrate (AN), prilling of NPK (16.5 : 16.5 : 16.5) and AN	$ 661.-
Sulphuric acid, phosphoric acid production, granulated NPK (17: 17 : 17) from phosphoric acid, nitric acid and ammonia	$ 745.80

The digestion of 1 ton P_2O_5 requires approximately 1 ton sulphur. The difference in production costs stems from the cost of this sulphur and the savings from raw materials and utilities consumption as outlined above, minus the slight difference in capital costs between the two process schemes.

8.4 Other significant differences between conventional and low-waste technologies

Phosphate rock quality

In principle, any quality of phosphate rock can be used as phosphate raw material, but for practical and economical process performance there will be certain limitations.

Apatite of igneous origin, as for instance Russian Kola phosphate, is generally well-suited to the process.

About 85 per cent of the world's phosphate rock production, however, consists of phosphate of sedimentary organic origin. In those types, minor quantities of organic material still remain. In the acidulation step, these will cause some reduction of nitric acid to NO_x and act as a foam stabilizer and cause vigorous foaming in connection with the formation of carbon dioxide. By calcination of the sedimentary phosphates, these problems are eliminated as organic matter is then destroyed and carbon dioxide driven out.

Considerable work has been done at our Research Centre and in test runs in the plants in order to try out phosphate rocks from all over the world. With suitable equipment design, the use of antifoaming agents and some training, even the uncalcined low grade ores can now be mastered.

Due to corrosion and the undesirable aspects of having nitric acid and chloride together at high temperatures, high chlorine containing phosphate rocks should not be used. We have found, however, that a chlorine content of up to 0.1 per cent can be tolerated. At this level, the passivity of CrNiMo 18-12-3 stainless steel is not destroyed. Rocks with considerably higher Cl-content may also be utilized if special precautions are taken.

If the rock contains much insoluble matter, this may be removed. The insolubles are mainly silica, and tend to cause erosion-corrosion of equipment such as pumps and valves. High contents of acid-soluble impurities such as iron, aluminium and magnesium, should be avoided, as these components tend to decrease the water solubility of the P_2O_5, and may cause process difficulties.

Such process difficulties are mainly caused by high viscosities in the neutralizers and following process steps. As a result of many years of research work and test runs, we are now able to minimize these problems by adjustment of process conditions.

In our plants, phosphate rocks of the following origin have during recent years been successfully used :
Kola, Israel (calc.), Florida (many varieties), North Carolina (calc.TGS), Togo, Senegal (Taiba), Spanish Sahara, Morocco and Sweden.

Storage properties

Norsk Hydro has been storing NPK in bulk at their Porsgrunn factory since 1948 and in Glomfjord since 1954. Also, NPK-fertilizers have been shipped in bulk to a number of markets such as India, Pakistan and United States, in addition to the traditional home markets like Denmark and Sweden.

All the bulk warehouses are ordinary concrete buildings which have not been specially treated or painted. All warehouses are situated close to the sea where the humidity is normally very high. Some of them have large doors opening directly to the outside. The only precaution taken is to keep the doors closed as much as possible. Provided the fertilizer has conformed to specification on leaving the factory, it has been found to remain free-flowing after six months or more of storage.

Suspension fertilizers

Liquid NP and NPK fertilizers in the form of suspensions are used in certain parts of the world.

Norsk Hydro has carried out extensive experiments on a technical scale which have proved that the neutralized liquor ("NP-liquor") from their process is a well-suited basis for making NP- and NPK-suspensions containing 25 to 30 per cent water. The successful experiments have covered a wide range of formulations and have in included production, then storage at low temperatures followed by spraying with commonly used equipment.

Self-sustaining decomposition

It is well known that compound fertilizers, containing ammonium nitrate and potassium chloride, will decompose when heated above initiation temperatures in the range of 150 to 230 °C.

For some formulations, the decomposition stops when the source of heat is removed. For others, however, the decomposition which has been initiated by the external heat will spread to the surrounding mass and move through the complete mass as a hot zone - a self sustaining decomposition is running.

The propagation velocity may be from 0.04 to 0.5 metres per hour in most cases.

By initiation from hot pipes, fires and welding, severe decomposition in fertilizer has occurred owing to the fact that the product has been liable to the self-sustaining decomposition. Norsk Hydro has done a considerable amount of work in studying the mechanism of self-sustaining decomposition. Today they know the formulations in which this effect might occur. Their knowledge can be presented in the form of a graph giving the stable formulations at different Ca/P ratios (Figure 9). It is clear that the lower the Ca/P-ratio, the less risk there is of decomposition.

NPK fertilizers often contain other plant nutrients such as magnesium, copper, sulphur, boron, etc. : a great deal of work has been done in studying the effect of these components on the self-sustaining decomposition. As a conclusion, it can be said that kieserite and rasorite tend to decrease the self-sustaining decomposition effect if the water solubility is above 80 per cent. The opposite effect occurs, however, at lower water solubilities.

Copper increases the self-sustaining decomposition effect for all water solubilities of the phosphorous content. Many of the most common NPK-fertilizers based on NH_4NO_3 and KCl will undergo self-sustaining decomposition in the presence of 0.1 per cent Cu.

Although precautions must be taken in handling and storage of NPK-products, they do not limit the availability and use of NPK-fertilizers. The additional costs of these precautions for handling and storage of NPK-fertilizers will be negligible in most countries.

Agronomic suitability

The crop response obtained when applying chemical fertilizers will to a certain extent depend upon the forms in which the individual plant nutrients are present in the fertilizer materials. The N- and P-components present in the fertilizer materials in question have the following main characteristics :

Typical composition

	N-component	P-component
(a) Granulated product from phosphoric acid, NH_3 and HNO_3	60% NH_4-N 40% NO_3^--N	Water solubility close to 100%
(b) Norsk Hydro Nitrophosphate product	55% HN_4-N 45% NO_3^--N	Water solubility Up to 85%

It appears that (a) and (b) are very similar with regard to the N-component which, for practical purposes, can be regarded as consisting of one half ammonical N and one half nitrate-N.

It is fairly well established that the efficiency of the two nitrogen forms are more or less equal when the fertilizer material is mixed with well-drained soil.

There are, however, situations where one of the N-forms is preferable to the other. The split N-component will be advantageous in fertilizing systems involving top dressing, and especially on grassland and on soils with rather high pH because the volatilization loss of N from a split component is lower than from a pure ammonical component. This is of particular importance under dry weather conditions. In paddy rice growing, the nitrate part of the N-component will be subject to losses through dentrification which, to a certain degree, limits the use of fertilizers having a split N-component in rice growing areas. Recent research in India indicated, however, that this type of N-component also can be utilized efficiently by irrigated rice when applied in split doses.

In looking at the P-component of the fertilizer materials in question, one finds that both contain the highly water-soluble form, which implies definite advantages when compared to multi-nutrient fertilizers of lower P-solubility and chemically untreated rock phosphates.

It is well established that on neutral- to alkaline soil the highest P-efficiency can be obtained from water soluble phosphorus, and considerable evidence is available to show that water soluble P- is equal to non-water soluble P on acid soils.

The high water-solubility of the P-component places both fertilizer types discussed here in the category of the most versatile fertilizers available today, inasmuch as they can be used over the widest range of soil-crop-climate conditions.

The K-component of NPK products should not need discussion here since the effectiveness of the added potassium salts will scarcely be influenced by the production process.

9. Reporting organization

Norsk Hydro A/S
P.O. Box 2594
Solli
OSLO 2
NORWAY

10. Date of Report

10 October 1979

TABLE 1

REFERENCE LIST

Following plants using Norsk Hydro technology are now in operation or under construction

Country	Client	Location	Commissioning	Design Capacity (Product)	Finishing	Design Formulation[a]	Product water Solubility
Norway	Norsk Hydro	Porsgrunn	1967	2500 t/d	Prilling	22-11-11	80-85%
	Norsk Hydro	Porsgrunn	1970	1200 t/d	Prilling	22-11-11	80-85%
	Norsk Hydro	Glomfjord	1970	2000 t/d	Granulation	22-11-11	80-85%
Hungary	Chemokomplex	Petfürdo	1975/76	2700 t/d	Prilling	22-11-11	85%
Romania	Romchim	Tirgu Mures	1975/76	2700 t/d	Prilling	22-11-11	85%
	Romchim	Craiova	1975/76	2700 t/d	Prilling	22-11-11	85%
	Romchim	Turnu Magurele	1976	2700 t/d	Prilling	22-11-11	85%
	Romchim	Arad	1977	2700 t/d	Prilling	22-11-11	85%
USSR	Techmashimport	Novgorod	1979	1850 t/d	Prilling	16.5-16.5-16.5	85%
	Techmashimport	Novgorod	1980	1850 t/d	Prilling	16.5-16.5-16.5	85%
	Techmashimport	Dorgobuzh	1980	1850 t/d	Prilling	16.5-16.5-16.5	85%
	Techmashimport	Pridonsk	1981	1850 t/d	Prilling	16.5-16.5-16.5	85%
	Techmashimport	Pridonsk	1981	1850 t/d	Prilling	16.5-16.5-16.5	85%
China	China National Technical Import Corporation (CNTIC)		1982	2970 t/d	Granulation	27-13-0	70%

---

[a] Most plants can produce other formulations as well such as 16.5-16.5-16.5, etc.

TABLE 2

Conversion of calcium nitrate to ammonium nitrate and calcium carbonate

Country	Client	Location	Commissioning		Finishing	Design Formulation
Norway	Norsk Hydro	Porsgrunn	1973	200t N/d	Solution	Ammonium nitrate
Hungary	Chemokomplex	Petfürdo	1975/76	350t N/d	Prilling	Ammonium nitrate
Romania	Romchim	Tirgu Mures	1975/76	500t N/d	Solution	Ammonium nitrate
	Romchim	Craiova	1975/76	500t N/d	Solution	Ammonium nitrate
	Romchim	Turnu Magurele	1976	500t N/d	Solution	Ammonium nitrate
USSR	Techmashimport	Novgorod	1979	350t N/d	Solution	Ammonium nitrate
	Techmashimport	Novgorod	1980	350t N/d	Solution	Ammonium nitrate
	Techmashimport	Dorgobuzh	1980	350t N/d	Solution	Ammonium nitrate
	Techmashimport	Pridonsk	1981	350t N/d	Solution	Ammonium nitrate
	Techmashimport	Pridonsk	1981	350t N/d	Solution	Ammonium nitrate
Ammonium nitrate/Ammonium nitrate limestone						
Norway	Norsk Hydro	Rjukan	1975	450 t/d	Granulation	Ammonium nitrate
				or 600 t/d	Granulation	Ammonium nitrate limestone (26%N)

TABLE 3

Sulphur based NPK

Raw materials and utilities
per metric ton P_2O_5 - conventional tech.

Input element	H_2SO_4	H_3PO_4	HNO_3	Granulation	Total
H_2SO_4, t/t P_2O_5	-	(2.85)	-	-	
H_3PO_4, "	-	-	-	(1.02)	
HNO_3, "	-	-	-	(1.80)	
NH_4NO_3 "	-	-	-	-	
Sulphur "	0.97	-	-	-	0.97
Phos.rock 33% "	-	3.15	-	-	3.15
CO_2 "	-	-	-	-	
NH_3 "	-	-	0.52	0.76	1.28
KCl "	-	-	-	1.67	1.67
Steam, "	2.85	2.40	-0.56	2.00	6.69
Water, "	99.8	175	306	-	580.8
Fuel, "	-	-	-	0.065	0.065
Electricity kW/T P_2O_5	17.1	75	18	282	392.1
Platinum g/t P_2O_5	-	-	0.027	-	0.027

Raw materials and utilities consumption per metric ton P_2O_5 Figures in parentheses indicate that they are represented elsewhere in the table as basic raw materials sulphur, phosphate, rock or ammonia.

TABLE 4

Nitrophosphate-based NPK

Raw materials and utilities per metric ton P_2O_5 - nitrophosphates

Input element	Nitrophosphate			AN credit		Total
	HNO_3	N-phos	subtot.	HNO_3	AN	
H_2SO_4 t/t P_2O_5	-	-	-	-	-	-
H_3PO_4 "	-	-	-	-	-	-
HNO_3 "	-	(4.44)	-	-	(2.62)	-
NH_4NO_3 "	-	(-3.40)	-	-	-	-
Sulphur "	-	-	-	-	-	-
Phos rock "	-	3.06	3.06	-	-	3.06
CO_2 "	-	1.06	1.06	-	-	1.06
NH_3 "	1.29	1.42	2.71	0.76	0.72	1.23
KCl "	-	1.64	1.64	-	-	1.64
Steam "	-1.38	6.50	5.12	-0.81	0.34	5.59
Water "	754.8	100	854.8	445	27.2	382.6
Fuel "	-	0.03	0.03	-	-	0.03
Electricity kW/t P_2O_5	44.4	530	574.4	26.2	153	395.2
Platinum g/t P_2O_5	0.067	-	0.067	0.039	-	0.028

Raw materials and utilities consumption per ton P_2O_5. Figures in parentheses indicate that they are represented elsewhere in the table as basic raw materials sulphur, phosphate rock or ammonia.

FIGURE 1

SULFURIC ACID PLANT–SINGLE CATALYSIS (Flow Rates per Ton 100% H_2SO_4)

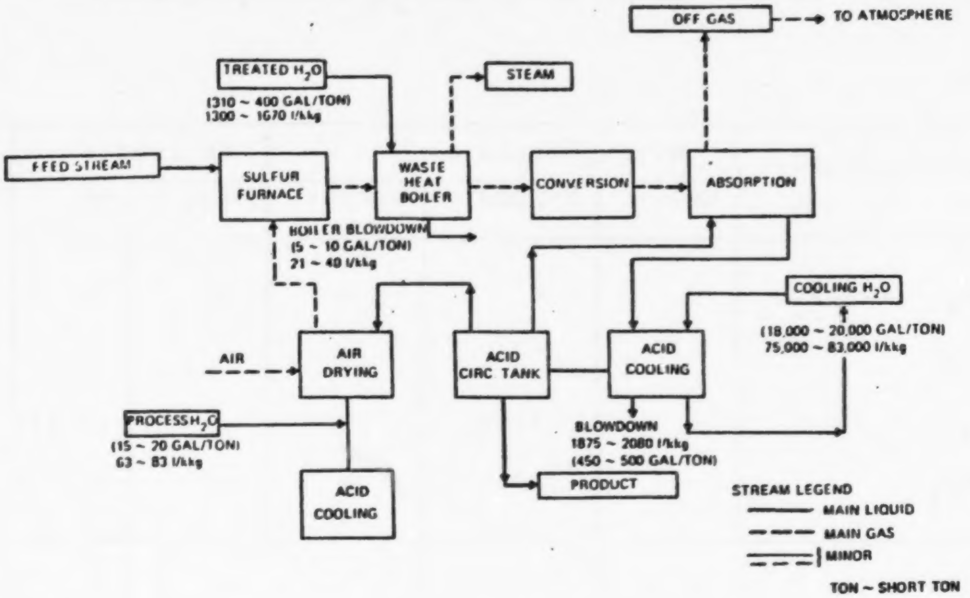

OFF GAS
TO ATMOSPHERE
TREATED H_2O
(310 ~ 400 GAL/TON)
1300 ~ 1670 l/kkg
STEAM
FEED STREAM
SULFUR FURNACE
WASTE HEAT BOILER
CONVERSION
ABSORPTION
BOILER BLOWDOWN
(5 ~ 10 GAL/TON)
21 ~ 40 l/kkg
COOLING H_2O
(18,000 ~ 20,000 GAL/TON)
75,000 ~ 83,000 l/kkg
AIR
AIR DRYING
ACID CIRC TANK
ACID COOLING
PROCESS H_2O
(15 ~ 20 GAL/TON)
63 ~ 83 l/kkg
BLOWDOWN
1875 ~ 2080 l/kkg
(450 ~ 500 GAL/TON)
PRODUCT
ACID COOLING
STREAM LEGEND
MAIN LIQUID
MAIN GAS
MINOR
TON ~ SHORT TON

FIGURE 2

WET PROCESS PHOSPHORIC ACID–H_2SO_4 ACIDULATION (Flow Rate per Ton P_2O_5)

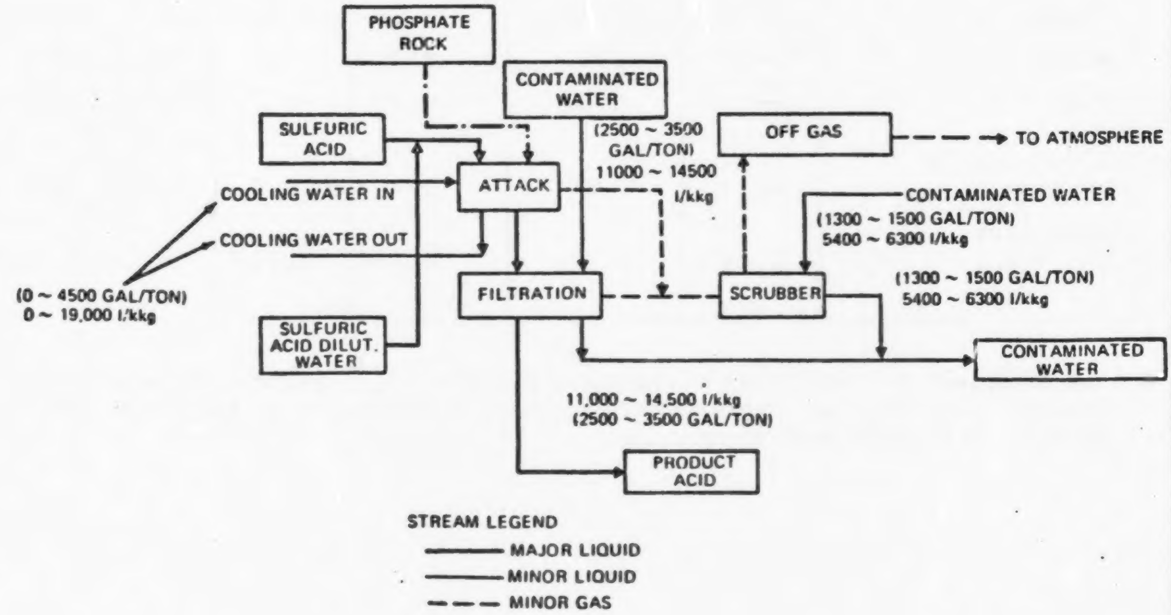

PHOSPHATE ROCK
CONTAMINATED WATER
SULFURIC ACID
OFF GAS
TO ATMOSPHERE
(2500 ~ 3500 GAL/TON)
11000 ~ 14500 l/kkg
ATTACK
COOLING WATER IN
COOLING WATER OUT
CONTAMINATED WATER
(1300 ~ 1500 GAL/TON)
5400 ~ 6300 l/kkg
(0 ~ 4500 GAL/TON)
0 ~ 19,000 l/kkg
FILTRATION
SCRUBBER
(1300 ~ 1500 GAL/TON)
5400 ~ 6300 l/kkg
SULFURIC ACID DILUT. WATER
CONTAMINATED WATER
11,000 ~ 14,500 l/kkg
(2500 ~ 3500 GAL/TON)
PRODUCT ACID
STREAM LEGEND
MAJOR LIQUID
MINOR LIQUID
MINOR GAS

Fig. 3

MONOAMMONIUM PHOSPHATE PLANT (Flow Rate per Ton) MAP

TON–SHORT TON

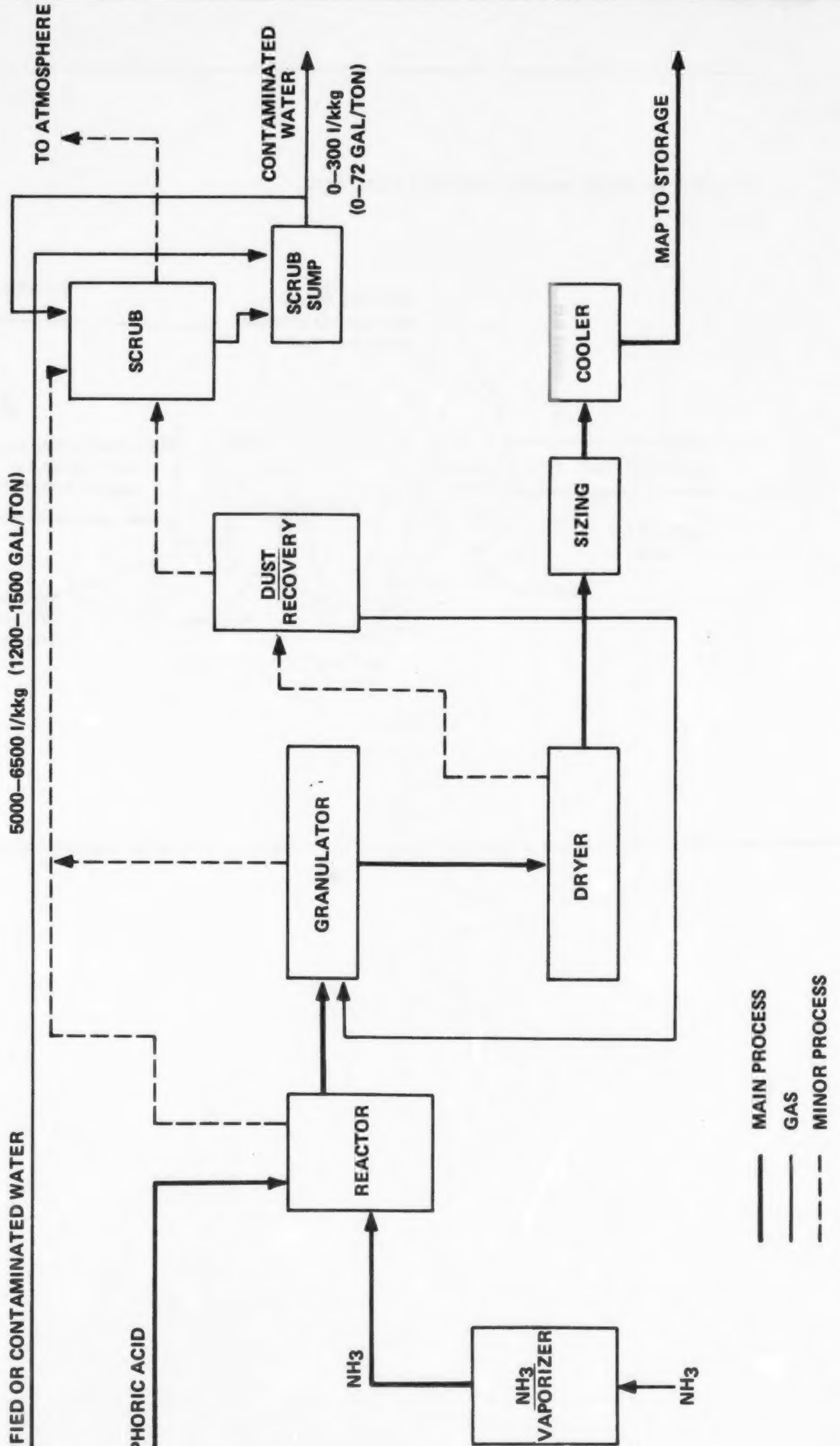

CLARIFIED OR CONTAMINATED WATER
5000–6500 l/kkg (1200–1500 GAL/TON)
TO ATMOSPHERE
CONTAMINATED WATER
0–300 l/kkg
(0–72 GAL/TON)
SCRUB
SCRUB SUMP
PHOSPHORIC ACID
NH3
NH3 VAPORIZER
NH3
REACTOR
GRANULATOR
DUST RECOVERY
DRYER
SIZING
COOLER
MAP TO STORAGE
MAIN PROCESS
GAS
MINOR PROCESS

FIG. 4

GYPSUM POND WATER SEEPAGE CONTROL

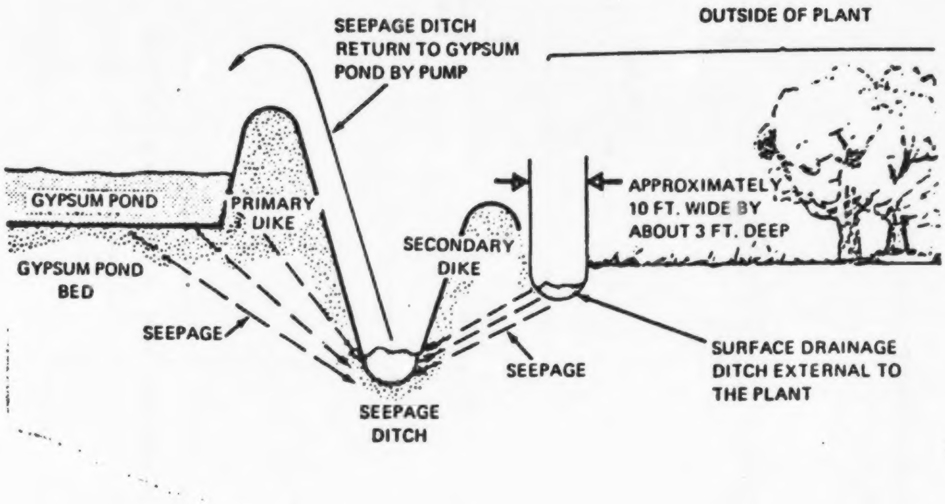
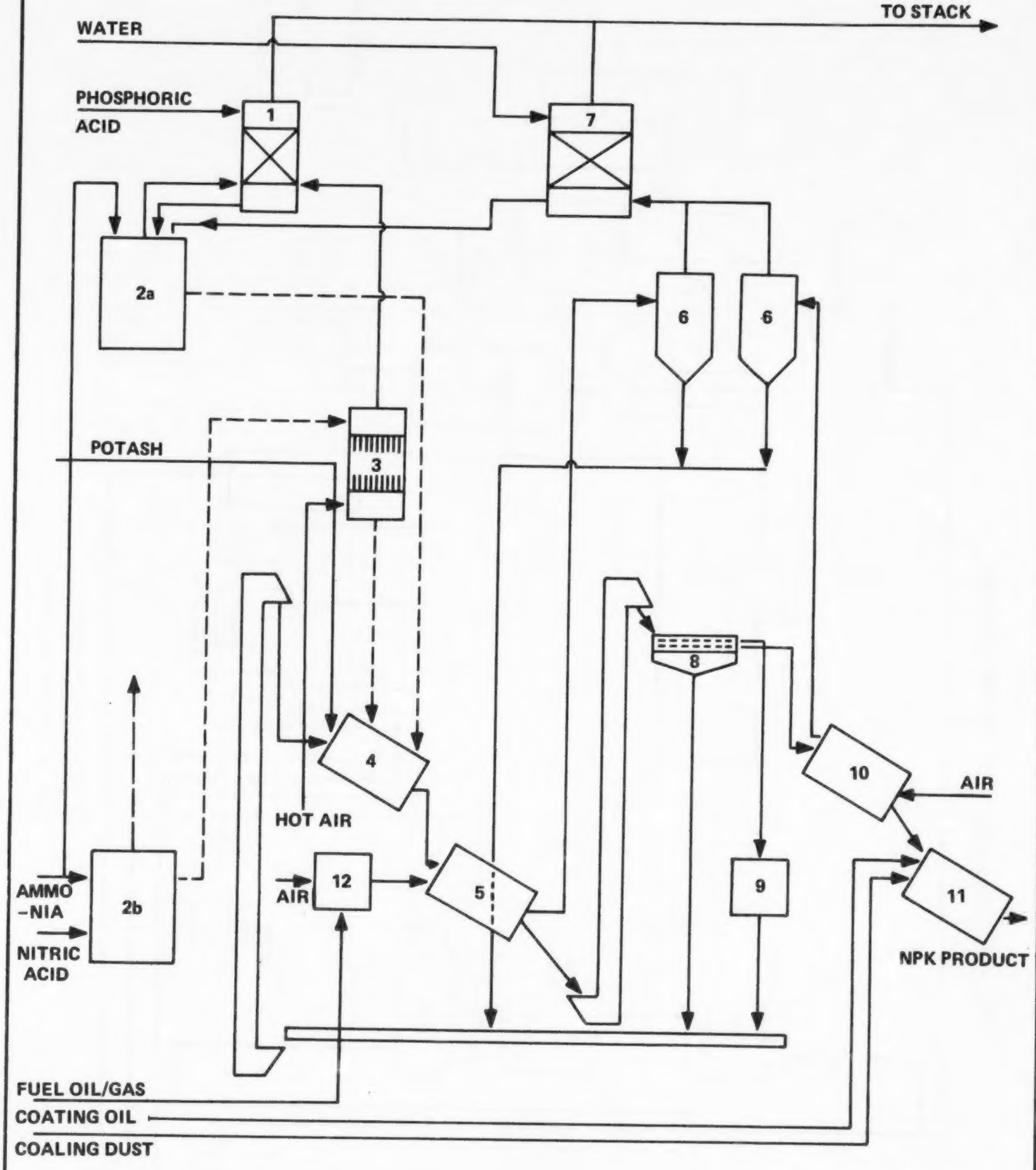

SEEPAGE DITCH RETURN TO GYPSUM POND BY PUMP
OUTSIDE OF PLANT
GYPSUM POND
PRIMARY DIKE
APPROXIMATELY 10 FT. WIDE BY ABOUT 3 FT. DEEP
SECONDARY DIKE
GYPSUM POND BED
SEEPAGE
SEEPAGE
SURFACE DRAINAGE DITCH EXTERNAL TO THE PLANT
SEEPAGE DITCH

Fig. 5

SULPHUR BASED GRANULATION PLANT

Granulation Process


WATER
TO STACK
PHOSPHORIC ACID
1
7
2a
6
6
POTASH
3
4
8
10
AIR
HOT AIR
12
AIR
5
9
11
AMMO -NIA
2b
NITRIC ACID
NPK PRODUCT
FUEL OIL/GAS
COATING OIL
COALING DUST

1	Phosphoric acid scubber
2a	Phosphoric acid neutralizer
2b	Nitric acid neutralizer
3	Evaporator
4	Mixer
5	Drier
6	Dust cyclones
7	Gas cleaner
8	Screens
9	Crusher
10	Cooler
11	Coating drum
12	Air heater

FIG. 6

Process flowsheet of NPK process

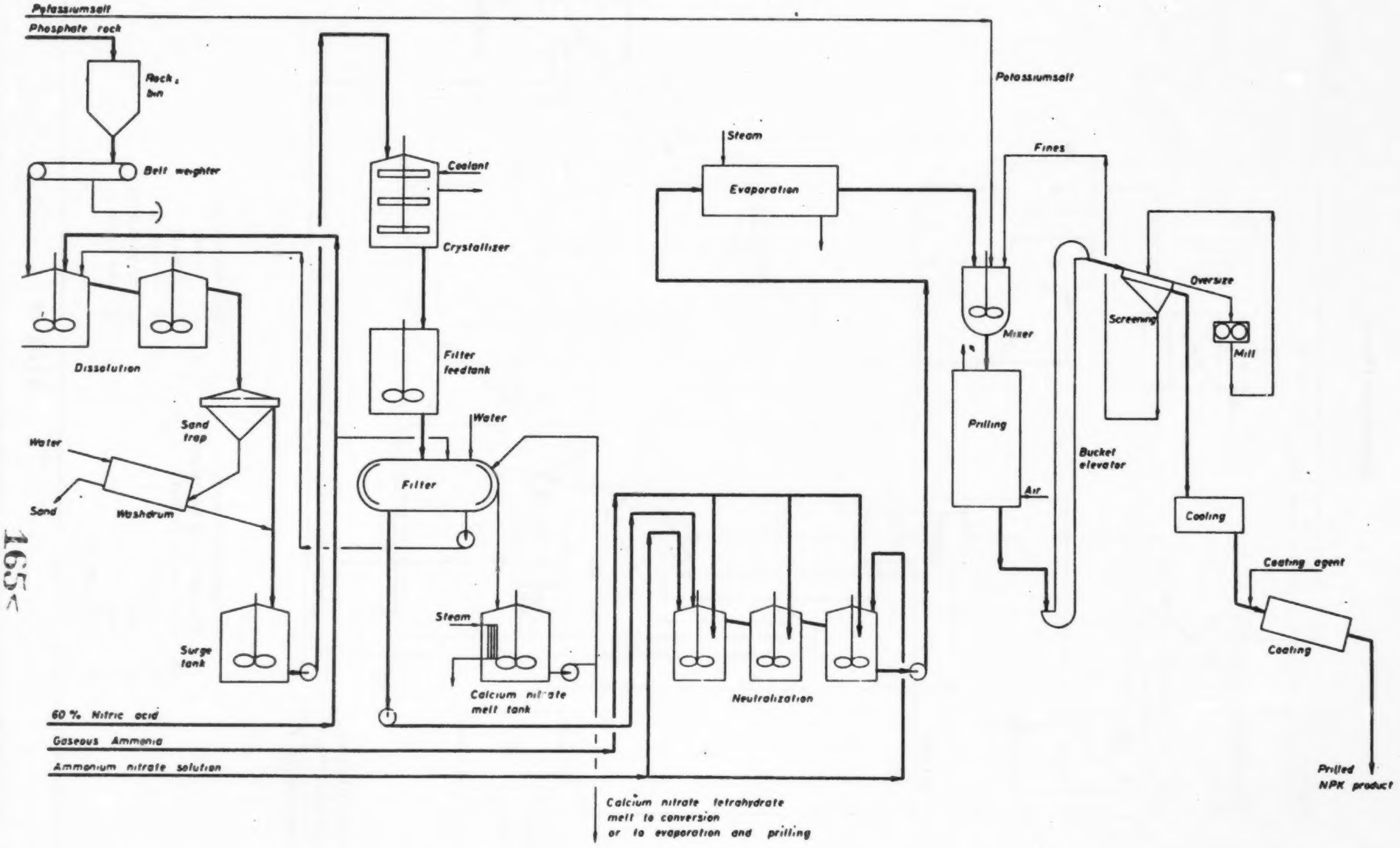

Potassiumsalt
Phosphate rock
Rock bin
Belt weighter
Dissolution
Sand trap
Water
Sand
Washdrum
Surge tank
60 % Nitric acid
Gaseous Ammonia
Ammonium nitrate solution
Coolant
Crystallizer
Filter feedtank
Water
Filter
Steam
Calcium nitrate melt tank
Calcium nitrate tetrahydrate melt to conversion or to evaporation and prilling
Neutralization
Steam
Evaporation
Potassiumsalt
Fines
Mixer
Prilling
Air
Bucket elevator
Screening
Oversize
Mill
Cooling
Coating agent
Coating
Prilled NPK product

FIG. 7

Conversion of Calcium nitrate melt to Ammonium nitrate solution

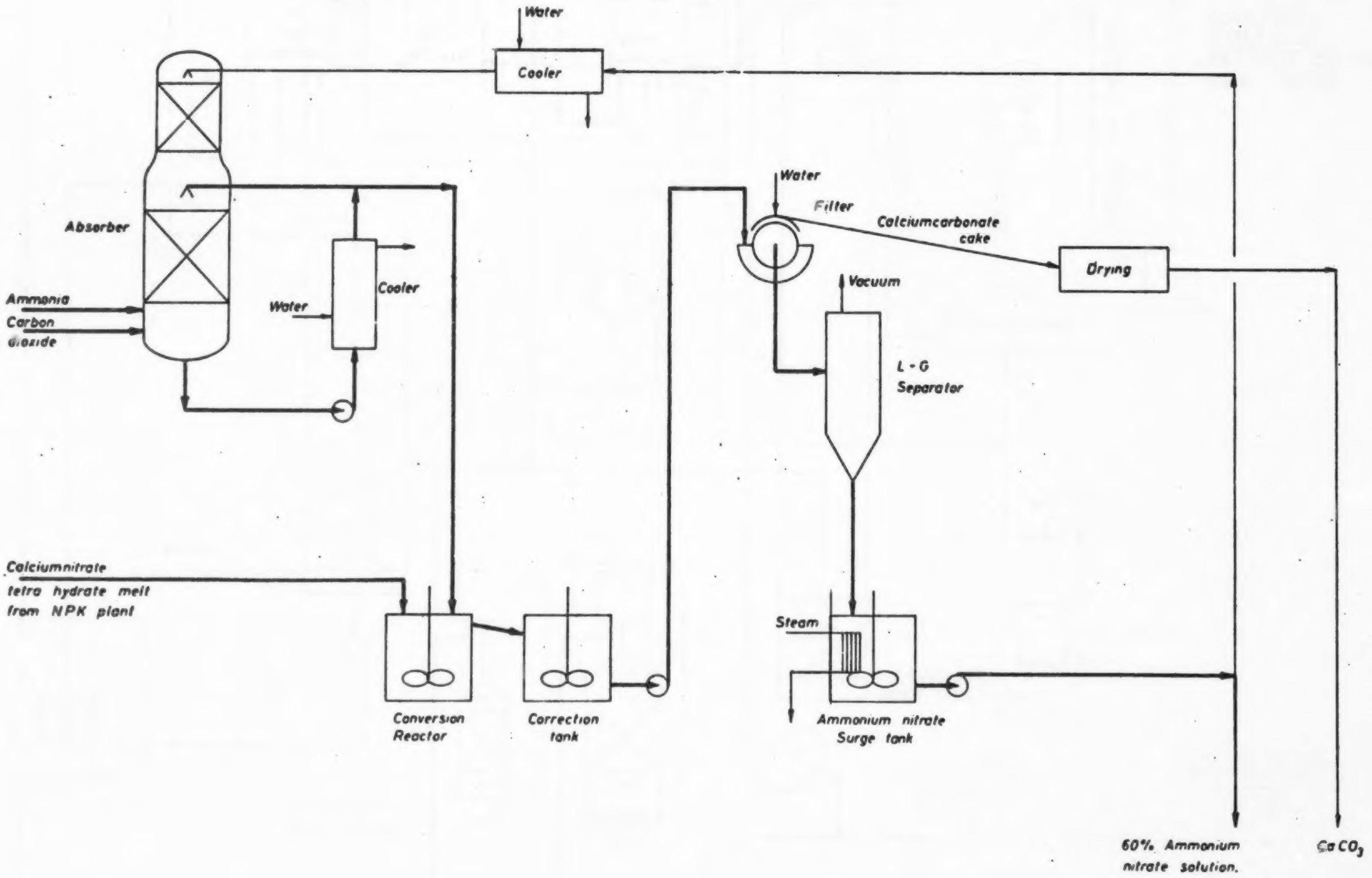
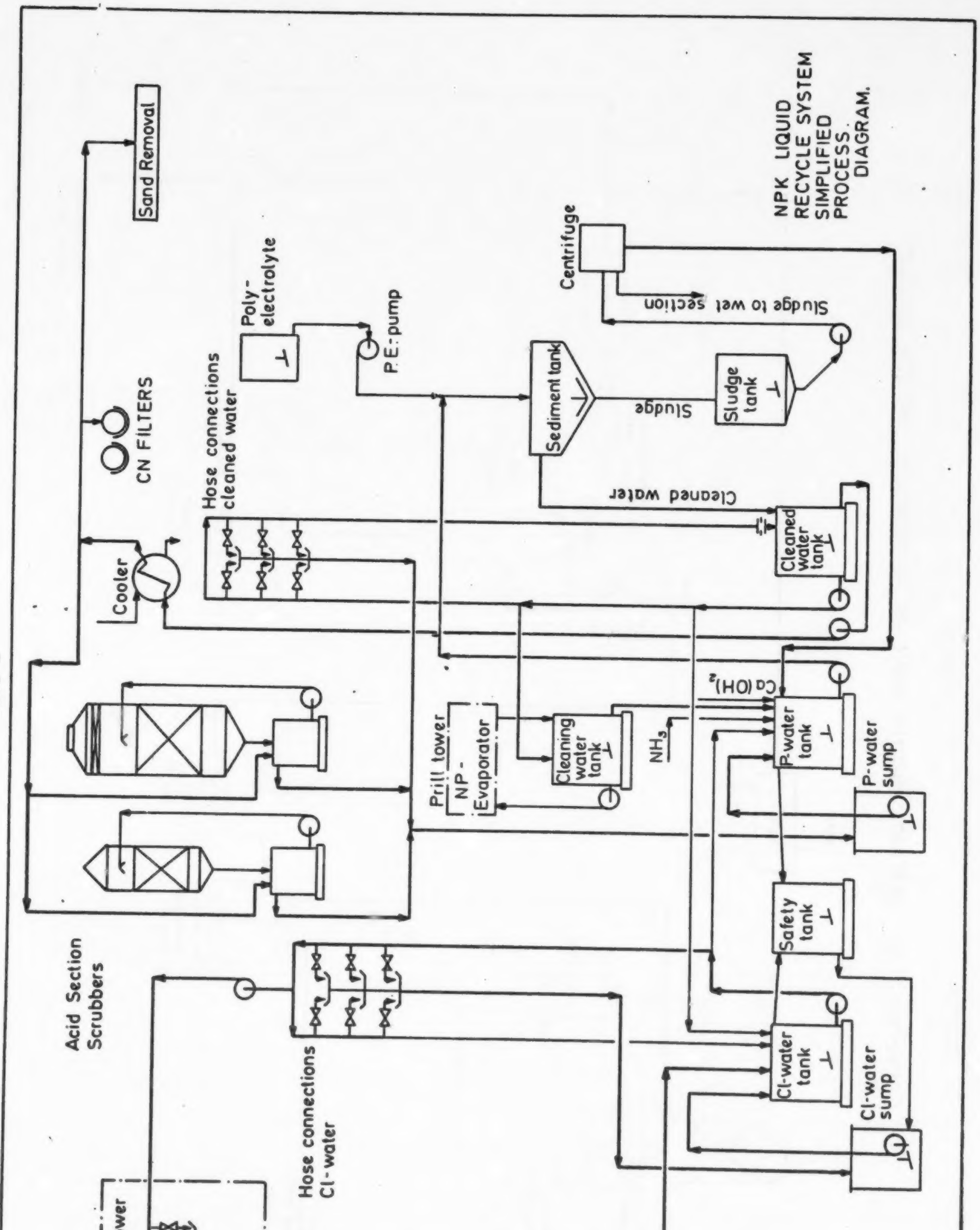
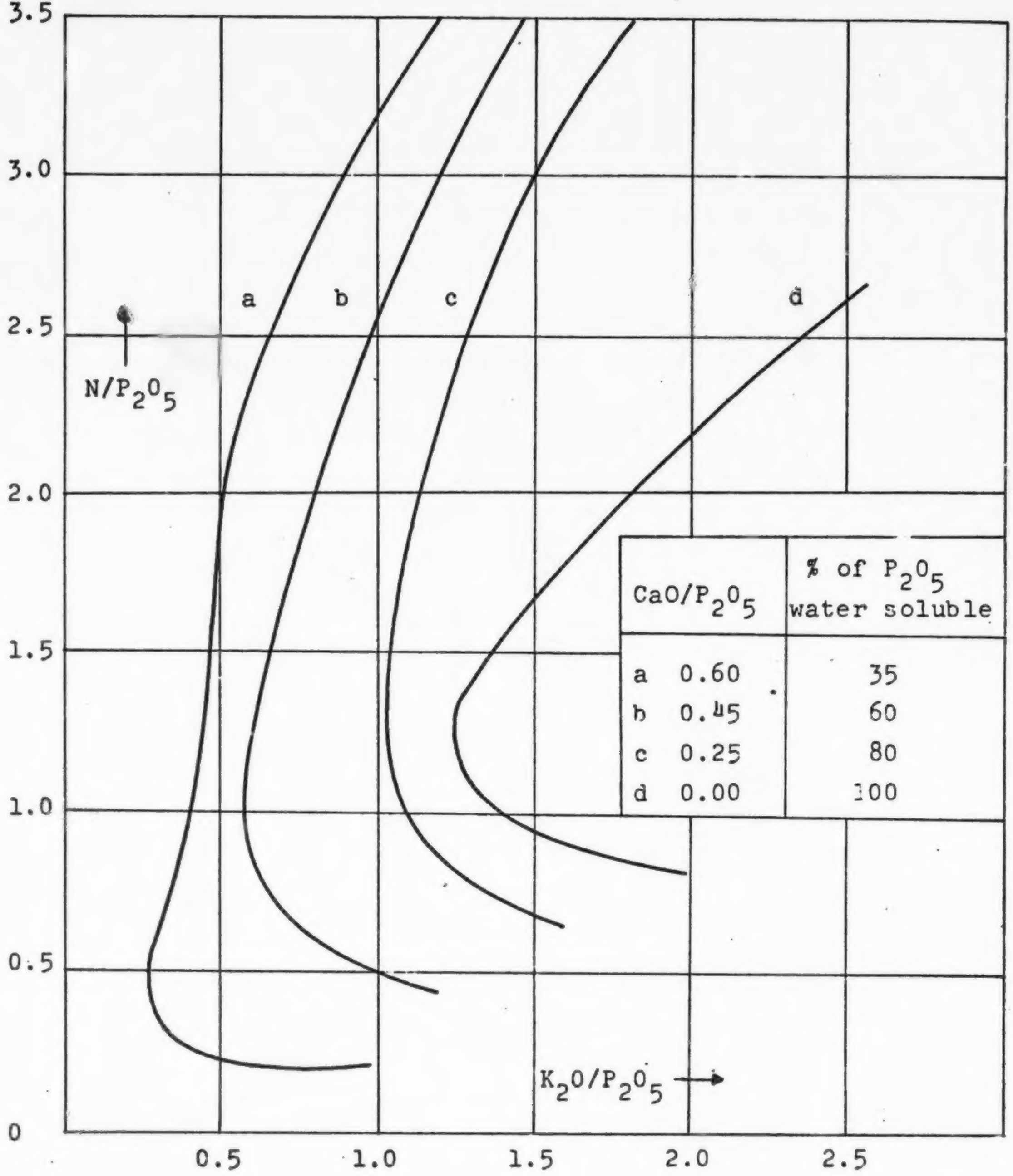

Water
Cooler
Absorber
Ammonia
Carbon dioxide
Water
Cooler
Calciumnitrate tetra hydrate melt from NPK plant
Conversion Reactor
Correction tank
Water
Filter
Calciumcarbonate cake
Drying
Vacuum
L-G Separator
Steam
Ammonium nitrate Surge tank
60% Ammonium nitrate solution.
CaCO3

FIG. 8


Sand Removal
CN FILTERS
Cooler
Hose connections cleaned water
Poly-electrolyte
P.E. pump
Centrifuge
Sludge to wet section
Sediment tank
Sludge
Sludge tank
Cleaned water
Cleaned water tank
Prill tower
NP-Evaporator
Cleaning water tank
NH$_3$
Ca(OH)$_2$
P-water tank
P-water sump
Safety tank
Acid Section Scrubbers
Hose connections Cl-water
Cl-water tank
Cl-water sump
Prill tower

NPK LIQUID RECYCLE SYSTEM SIMPLIFIED PROCESS. DIAGRAM.

FIG. 9



EFFECT OF WATER SOLUBILITY OF P_2O_5
ON PRODUCT STABILITY

The products contain ammonium nitrate, potassium chloride, and ammonium- and calcium phosphate. Self-sustaining decomposition occurs to the right of the curves.

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

RESTRICTED

ENV/WP.2/5/Add.12
10 July 1981

ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE
SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW - AND NON-WASTE TECHNOLOGY

Monograph

SEMI-CLOSED OR CLOSED SILICON/FERRO-SILICON FURNACES WITH GAS CLEANING AND HEAT RECOVERY

Transmitted by the Government of Norway

1. Identification of industry

Silicon/Ferrosilicon. ISIC code 1/ : 3720

2. Basic characteristics of the production process

The general design of reduction furnaces employed in the smelting of the bulk types of ferroalloys is basically the same.

The essential job assigned to the reduction furnace is to supply the high temperature and energy for the chemical reactions required. Reaction products are to be smelted and superheated so that they can be readily drained through the furnace tap-hole and poured for casting. Raw materials are fed onto the top of the furnace. Power is applied to the electrodes which stay buried in the charge, and heat is dissipated in the reaction system through resistance, and arcing from the tip of the electrodes.

Gases and vapours generated in the reaction zones surrounding the electrodes escape through the furnace charge. A certain amount of heat is exchanged between hot gases and descending solids. The gas eventually rising out of the top is rich in carbon monoxide and carries fumes from the high temperature regions of the furnace. It also entrains finer sized constituents of the charge.

1/ International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex).

3. Name of conventional processing technology

Open top furnace with or without bag house filter.

4. Description of conventional processing technology

Until recently the reduction furnaces for silicon/ferrosilicon were built with open tops only and with an entirely uncontrolled waste gas system. In this design, the combusted gases are collected by a furnace hood and vented through stacks to the atmosphere. Through natural draft the burned reaction gas is diluted and cooled with large quantities of air leading to large stack gas volumes of moderate temperature. Conventional furnace hood design will admit stack gas volumes in the range of 15 to 20 Nm^3/kWh. Consequently, a medium sized 20 MW ferrosilicon furnace will emit waste gas at a rate of 300 to 400,000 Nm^3/h. Of this volume the actual reaction gas accounts for only about 2 per cent. Emission from such an open top furnace is, for all practical purposes, just hot air, except that it entrains particulate matter in the low concentration range of 1 to 4 g/Nm^3.

The solids, being mostly fumes in sub-micron sizes, cause a highly visible emission. An open top furnace is easily recognized as a heavy polluter, and efficient gas cleaning is difficult and expensive. Faced with the problem of cleaning the extremely large volumes of gas emitted from open top furnaces, ideas on ways and means for limiting the quantity of air immediately spring to mind. For various reasons dry-filtering in bag-house type equipment is considered to offer the most appropriate solution so far on the cleaning side. Since filter investment and operating costs, as well as filter power consumption, are approximately proportional to volumetric gas flow, measures for reducing volumes are particularly rewarding.

In existing, conventional furnace design there are usually limited possibilities for a closer hooding due to the fact that a reduction of the dilution air volume will cause a temperature rise which is detrimental to the equipment.

5. Name and state of development of low- and non-waste processing technology

(a) Semi-closed furnace with waste heat boiler and filter, industrial scale,

(b) Closed furnace with filter and gas-fired boiler - small industrial furnace developed; filter installed in 1979.

6. Description of low- and non-waste processing technology

(a) Semi-closed silicon/ferrosilicon furnace

The first step towards the semi-closed furnace was the design of the low-hood type. On this type of furnace there is a concentration of equipment above the hood roof, away from the heat. Simplicity and sturdiness characterize the arrangement underneath the hood. The semi-closed furnace can be described as a low-hood furnace equipped with hood side-walls extending to the top of the furnace body, and movable doors to allow access for stoking, etc. This furnace type is designed for high temperatures, and hence for reduction of the dilution air volume; it offers ar the same time improved working conditions due to closer hooding.

Reduction of the smoke volume to be cleaned made possible by the semi-closed furnace, reduces the cost of cleaning. However, to bring the smoke temperature below the limits set by the filter bag material, cooling becomes necessary.

A gas-to-air heat exchange arrangement has been frequently used in the past. Today the trend is to raise the temperature of the gas to from 800 to 1200°C and to use a waste heat boiler to handle the dual task of recovering the energy and cooling to a temperature acceptable to the bags.

(b) Closed silicon/ferrosilicon furnace

By definition the closed furnace has a gas-tight cover so that the reaction gases are drawn off unburned. The gas volumes will thus be small, down to 2 per cent of the volume from open top furnaces.

The small gas volume to be cleaned is one attractive aspect of the closed furnace. Another is that the unburned gas represents a more valuable resource than the burned gas, and offers more flexibility in usage:

- heating purposes;
- production of steam for heating purposes or for production of electrical power via a steam turbine;
- process gas for chemical processing.

Due to these advantages the closing of a ferrosilicon furnace has attracted attention over the last few decades.

What them are the reasons for the slow progress in closing the high-grade ferrosilicon furnace, bearing in mind that the closed furnace is the normal choice for practically all other electro-metallurgical products? The main drawback is to be found in the characteristics of the silica-carbon reaction system in which condensing and escaping of silicon-monoxide easily leads to gas blows and crust formations as well as high losses and temperatures. Free access to the furnace top for stoking has, therefore, always been a must in order to maintain a good operation on high-grade ferrosilicon.

When Elkem-Spigerverket SA decided to start the closed ferrosilicon furnace project in 1974, new means for stoking the charge mix in the furnace had to be developed. Conventional stoking through gas-tight seals in the cover was subjected to a thorough study. Parallel with this evaluation, work was started on a completely new concept without stokers, but where the furnace body was given a special design. From Figure 1 it may be seen that the furnace body has been divided in two parts, one lower and one upper, the interior cross-section of the upper part being given the shape of a regular polygon, typically with nine sides. The bottom part, which is the main furnace body, and the upper part, which is referred to as the ring, may be rotated independently of each other. In principle, any combination of rotation or oscillation of the two bodies may be applied.

The effect of the split furnace operation is a bulk effect in the charge, transplanted radially inwards from the circumference, and downwards from the top surface. An indication of these effects can be seen when observing the furnace top. Visual observation can, however, only give a vague indication of the total effect on the charge. Due to different velocities of the upper and lower parts of the split furnace body, the charge around the dividing plane between the parts will be exposed to a shearing/kneading effect which results in a non-sticking, porous charge.

An open furnace of 6.5 MW capacity at Bremanger Smelteverk was chosen for conversion to a completely closed furnace for operation on 75 per cent ferrosilicon.

Test operation on this furnace was started in 1977. After the first half year of adjustment of equipment and refining of the process, the furnace has been operated without major problems. In fact, the furnace for some time now has been looked upon as a regular production unit.

The furnace has so far been operated without gas cleaning. Typical gas analyses are: CO 65 to 80 per cent, CH_4 0 to 4 per cent, H_2 12 to 25 per cent, N_2 1 to 3 per cent. The dust particles are larger than the particles from an open furnace, and they have a tendency to form aggregates which makes the dust from a closed furnace more easy to precipitate, for instance in a wet scrubber. Cleaning in wet venturi scrubbers has been tried, and is an established technology, but the method is not encouraging due to the sophisticated sludge and water treatment required to comply with pollution standards.

For the closed ferrosilicon furnace, the strategy has been to verify two alternative methods of handling the gases:

(i) Dry filtering of the CO-rich gas:

- Promising tests in a small test unit were accomplished.
- A full-scale filtering unit was constructed for start up in 1990

The cleaned gas can be used as:

- process gas for chemical processing.
- fuel for steam boiler to produce steam for heating purposes or for production of electrical power via a steam turbine.

(ii) Burning the uncleaned, CO-rich gas in a specially developed steam boiler:

- Promising tests in a small test unit have been accomplished.

The steam produced can be used for heating purposes or for production of electrical power via a steam turbine. The burnt and cooled gas leaving the steam boiler can be cleaned in a bag house filter.

(c) Energy recovered with low-waste technology

The most efficient use of the recovered energy would be to utilize the steam for heating purposes or, for the closed furnace alternative, to utilize the CO-rich gas as a fuel for chemical processing. Such solutions are known, but the condition is a favourable plant location where the neighbouring industries are big consumers of either steam, hot water or process gas. Due to secluded locations, however, there is often no other option than to convert the gas to electric power. By doing so, roughly two-thirds of the energy in the steam is lost in condensation of the exhaust steam from the turbine, in line with what is normal for steam power plants.

The percentage of energy recovered of electrical input to the furnace will be in the range of:

- 65 to 70 per cent with steam as the end product.
- 20 to 25 per cent with electrical power as the end product.

The type of reductants and mode of operation will influence these amounts.

So far we have had no practical experience in producing steam or electricity with gas from a closed furnace. Theoretical evaluations indicate that energy recovery based on CO-rich gas from the closed furnace will be more efficient than recovery from a semi-closed furnace.

6.7 Cost-related data intended to permit comparison of low- and non-waste technology with conventional technology.

The major stages in the development of the ferrosilicon furnace - leading up to the closed type - is illustrated in a simple way below.

(i) OPEN FURNACE

(ii) OPEN FURNACE WITH BAG HOUSE FILTER

(iii) SEMI-CLOSED FURNACE WITH BAG HOUSE FILTER

(iv) SEMI-CLOSED FURNACE WITH ENERGY RECOVERY SYSTEM AND BAG HOUSE FILTER

(v) CLOSED FURNACE WITH GAS CLEANING AND ENERGY RECOVERY SYSTEM

A natural question to ask at this point is, What main factors have caused this development to happen? One of the most important factors behind the chain of development has probably been the various countries' introduction of strict regulations on air- and water pollution control, forcing the metallurgical industry to change the regular concept of a standard metallurgical plant lay-out. Furthermore, the recent invention of the split furnace body has put the last stage - the closing of a commercial high grade ferrosilicon furnace - within reach. This has been a challenge to the industry for more than 25 years after the first tests to collect unburned gas from a 75 per cent ferrosilicon furnace were carried out in Norway back in 1950.

As one can see, the introduction of stringent air pollution control triggered off a chain of events which obviously aided by the industry's natural wish to reduce cost in a world where energy, manpower and equipment costs have a tendency to go in one direction only, namely upwards. Strict regulations have been imposed on water pollution. The next step will be the development of a low cost, dry system for cleaning the gas from closed ferrosilicon and silicon metal furnaces, and a considerable amount of effort is being directed by Elkem-Spigerverket sa towards this goal today.

To produce efficiently at low cost is a key to any industry's success and growth. In the production of 75 per cent ferrosilicon, the major cost items are : raw materials; electrical energy; labour. These account for more than 80 per cent of the total cost. Consequently, alterations in the design itself can only slightly contribute to a saving in the production costs. The relative importance of the three items will obviously vary with the unit cost of each one. Labour and electrical energy are probably the two items which show most variation from one country to another. In Norway, the cost of total manpower and cost of electrical energy will be roughly the same at a unit price of approximately 5.5 mills per kWh based on the production of 75 per cent ferrosilicon. With increasing power costs, it follows that energy recovery systems represent obvious cost-saving factors to consider for the electro-metallurgical industry to be able to meet today's keen competition.

When considering the five furnace types and combinations referred to earlier, how does the cost vary in the production of one ton of 75 per cent ferrosilicon? Based on a 20 and a 40 MW furnace and a unit price of 10 and 30 US mills per kWh respectively, the picture will be as shown in Figure 2 using the closed furnace with energy recovery system, as a reference of 100 in each case. From this figure one can draw the following conclusions: The higher the power cost, the more savings through energy recovery; The closed furnace with energy recovery is the most economical solution.

7. Schematic comparison between the conventional and the low- and non-waste technology

Not reported

8. Identification of needs for further research and development with regard to the low- and non-waste technology.

Not reported

9. Reporting Organization

Elkem-Spigerverket a/s
Oslo, Norway

10. Date of report

November 1, 1979

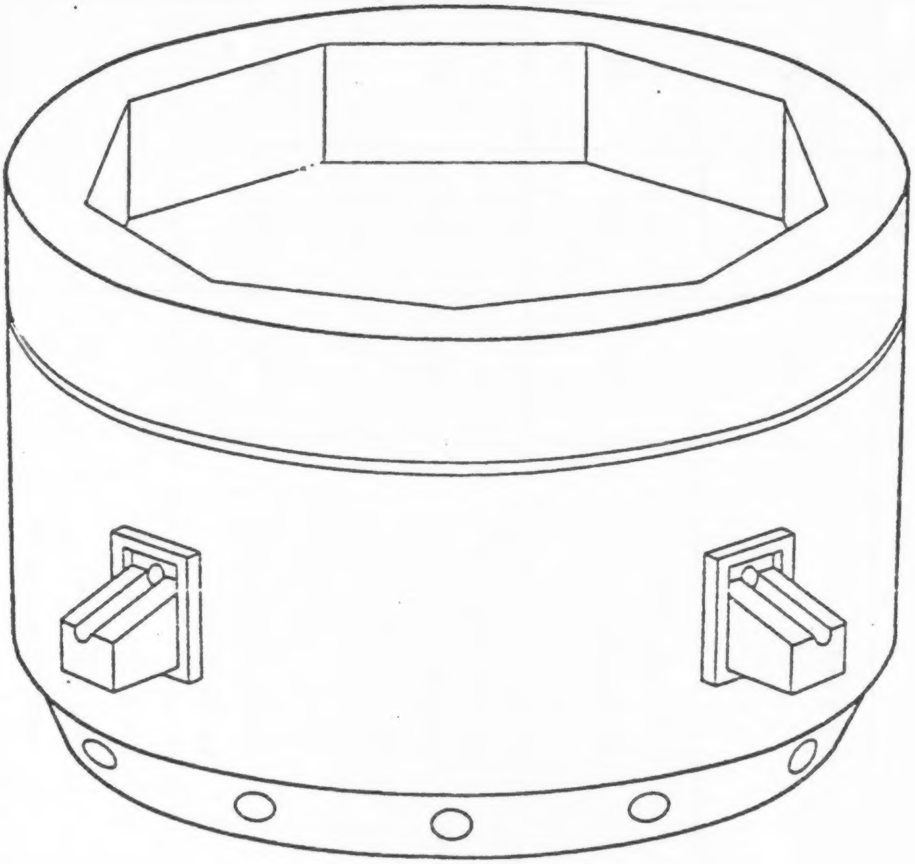
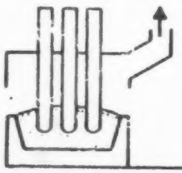
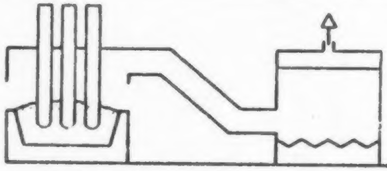
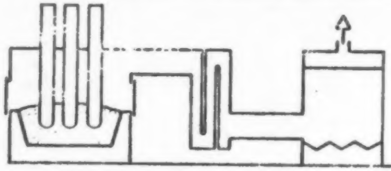
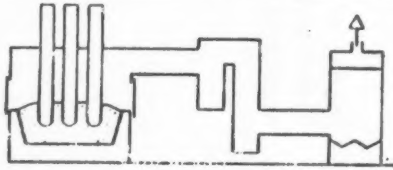
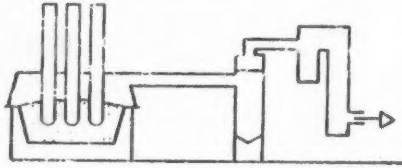


Figure 1 Model of The ELKEM Split Furnace Body. Any combination of rotation or oscillation of the upper and lower bodies may be applied.

FIG. 2

RELATIVE COST FIGURES FOR PRODUCTION OF 75 PER CENT FERROSILICON

		20 MW F'CE		40 MW F'CE	
		US mills per KWh		US mills per KWh	
		10	30	10	30
	OPEN FURNACE	100	109	102,5	112
	OPEN FURNACE BAG FILTER	106	114	108	117
	SEMICLOSED F'CE COOLER BAG FILTER	105	113	107	116
	SEMICLOSED F'CE ENERGY RECOVERY BAG FILTER	103	104	103	104
	CLOSED FURNACE GAS CLEANING ENERGY RECOVERY	100	100	100	100
CONVERSION FACTOR GIVING THE RELATIVE COST OF THE FOUR ALTERNATIVES		1,20	1,54	1,00	1,34

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

RESTRICTED

ENV/WP.2/5/Add.13
13 July 1981
ENGLISH ONLY

COMPEDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

RECOVERY OF FLUORIDES IN ALUMINIUM PRODUCTION (PRE-BAKED ANODES) BY IMPROVED GAS COLLECTION (HOODING) AND DRY SCRUBBING OF GAS

Transmitted by the Government of Norway

1. Identification of industry

Primary aluminium smelting . ISIC code [1]: 3720

2. Basic characteristics of production process

Commercial production of aluminium is generally accomplished by the electrolysis of a fused salt bath. The cells used to produce aluminium are comprised of carbon anodes and a bath material of cryolite ($Na_3Al\ F_6$), alumina (Al_2O_3), aluminium fluoride ($Al\ F_3$) and calcium fluoride (CaF_2). A direct current is used to decompose the alumina into aluminium. Because of its higher weight, the aluminium remains molten below the bath mixture and can be tapped off periodically. Cells are of four basic types: (a) the centre-worked prebake - CWPB, (b) the side-worked prebake - SWPB, (c) the vertical stub Soederberg - VSS, and (d) the horizontal stub Soederberg - HSS.

The prebake cell consists of a carbon lining or cathode and a number of anodes usually installed in two rows extending the length of the cell. The Soederberg cell consists of anodes which are in part baked and in part fluid paste.

3. Name of conventional processing technology

The Hall-Heroult process.

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex)

Reproduced from best available copy.

4. Description of conventional processing technology

Emissions from aluminium reduction cells occur in gaseous, solid and liquid form. Gaseous emissions include large quantities of carbon monoxide and dioxide, and smaller quantities of hydrogen fluoride, sulphur dioxide, carbon disulphide, silicon tetrafluoride, carbon tetrafluoride, hexafluorothene and water vapour. Among these emissions, hydrogen fluoride emissions have so far received the largest attention. Solid waste discharges include alumina, cryolite, aluminium fluoride, calcium fluoride, chiolite, carbon and iron oxide. Liquid discharges include entrained water and tar fog.

The amount of airborne residuals released depends upon process variables such as temperature, composition of the bath and the method of working the pots. During the reduction of aluminium, these emissions vary depending upon the type of anode and method of production. In addition, there can be large temporary increases in emissions, e.g., crust breaking for the periodic addition of alumina can increase fluoride emissions to 50 kg per metric ton of aluminium. Also if the alumina content is allowed to fall below a certain level, gas formation at the anode increases the resistance and thus the cell voltage. The resultant power increase is converted into heat which raises the temperature of the electrolyte. Subsequent breaking of the crust and addition of alumina at these higher temperatures can temporarily increase the fluoride evolution to a rate of 350 to 400 kg per metric ton of aluminium.

Reported data on fluoride evolution from existing aluminium facilities show wide variations between different plants and types of pots. An OECD survey indicated a range of 12 to 33 kg F/ton Al for prebake pots and 10 to 23 kg F/ton Al for vertical Soederberg pots. A survey of United States facilities indicated a range of 13 to 32 kg F/ton Al for prebake pots, 13 to 23 kg F/ton Al for vertical Soederberg pots and 20 to 23 kg F/ton Al for horizontal Soederberg pots. A survey of the International Primary Aluminium Institute (IPAI) on fluoride emission control on "typical" new plants indicated that a fluoride evolution of 12 to 20 kg F/ton Al for prebake pots, 19 to 20 kg F/ton Al for vertical Soederberg pots and 17 to 19 kg F/ton Al for horizontal Soederberg pots could be achieved.

The effective control of fluoride emissions from aluminium pot-lines includes:

(a) collection of gas from cells,

(b) removal of fluoride from the collected stream of gas, and

(c) removal of fluoride from the ventilation air.

Reproduced from best available copy.

Each of the cell types used has an upper limit to the collection efficiency because its physical construction limits the effectiveness of the hooding that can be used. For some plants, the upper limit of efficiency cannot be attained without expensive redesign of cells and hooding. Moreover, within a given class of cells, i.e. HSS, achievable collection efficiency depends upon the specific cell geometry. The actual collection efficiency is dependent upon the design of the "cell hood system".

While collection efficiency is specific to a particular design, some general observations on achievable efficiencies for different cell types can be made. On the centre worked prebake cells, the hooding consists of removable end doors and a series of segmented side doors. In a fully automated operation, normal production, crust breaking and raw material additions can be accomplished within a closed cell. However, the end doors would be removed for metal tapping and bath/metal control, and during change of anodes the side doors would be removed. While the primary collection efficiency would be less during operations requiring removal of the doors, a long-term average collection efficiency of 95 per cent or better can be achieved. For the side worked prebake cell, the necessity of removing the side covers during the crust breaking and anode changes is largely responsible for reducing the long-term average primary collection efficiency to from 80 to 85 per cent. Efficiencies of up to 90 per cent or more can be achieved in practice if suitable hoods and fast operating processing machinery (e.g. wheel type crust breakers) are used. The horizontal Soederberg cells can be designed for a primary collection efficiency in the low 90 per cent range. Vertical stub Soederberg cells have a low primary collection efficiency ranging from 80 to 85 per cent, because their operational procedure prohibits the use of hood skirts which completely cover the cell surface.

The removal efficiencies of the different pollution control devices that have been used on aluminium reduction facilities are shown in Table 1.

As can be seen from Table 1, the most efficient type of equipment for primary control of solid fluorides from prebake pots are based on the principle of dry scrubbing. The dry scrubbing technique is based on the reaction between hydrogen fluoride and alumina. The alumina is added to the pot gas before it passes through the filter which serves to arrest this alumina which then contains the absorbed and chemisorbed hydrogen fluoride and other particulate matter. The amount of alumina required will depend upon its chemical and physical properties. A major advantage of the process is that the fluoride components recovered are in a dry state and can therefore be fed directly back to the pots along with the alumina, thereby enabling a considerable saving in operating costs.

At present, there are two main types of alumina on the world market, i.e. the sandy type, and the floury type. The former is a coarse type with a low angle of repose (32° to 33°), the latter has a large particle range and an angle of repose of at least 42°. There are two important properties for an alumina feed to make it a suitable scrubbing agent for hydrogen fluoride, namely:

(a) the specific surface area, and

(b) the alpha content.

The specific surface area indicates to a certain extent the available area for the absorption of hydrogen fluoride. The sandy type of alumina generally has a specific surface area between 40 and 60 m^2/g and the floury alumina between 2 and 10 m^2/g. Since it is recommended to use an alumina with a specific surface area in excess of 32 m^2/g, floury alumina is not suitable for dry scrubbing.

During calcination of alumina, the crystalline structure changes from the very active gamma-alumina to the inactive alpha-alumina. The usual calcination temperature is about 1,050° C, resulting in about 50 per cent alpha-alumina.

It is recommended that the alumina to be used for dry scrubbing should have an alpha-content not exceeding 60 per cent. The trend towards a lower degree of calcination even among the traditional producers of high-alpha alumina, reflects an increasing interest in the dry scrubbing technique throughout the world. Originally the dry scrubbers were designed to allow for the whole alumina feed to the potlines to be passed through the scrubber. However, due to the pick-up of various trace elements from the exposed alumina (having detrimental effect upon the metal quality) Ardal og Sunndal Verk A.S. in Norway decided to try to reduce the alumina in the dry scrubber to a minimum. A reactor was designed and, after a successful trial at a pilot plant, a full-scale reactor was incoporated into the dry scrubbing installation at Sunndalsøra.

5. Name and state of development of low- and non-waste processing technology

The ASV dry scrubber/reactor is in the commercial stage of development.

The main objective of the reactor is to increase the residence time of gas/alumina and thereby reduce the amount of alumina needed in the dry scrubber. With a reactor it is possible to achieve a scrubbing efficiency of about 99 per cent with an alumina feed which is 30 per cent of the pot's requirements. Test runs have indicated that with a 30 per cent alumina feed to the dry scrubber while omitting the reactor, a scrubbing efficiency of only 93 per cent will be obtained. Such a scrubbing efficiency is too low to satisfy modern standards.

The main advantages of the reactor are the following two properties:

(a) Satisfactory scrubbing efficiency can be achieved with an alumina feed as low as 15 to 20 per cent.

(b) The reactor with discharge orifice at the bottom splits the alumina stream in such a way that the alumina with only minor contamination exits at the bottom, while the heavily contaminated portion goes into the filter. The heavily contaminated portion, which contains 70 to 100 per cent of the recycled trace materials including Na_2O, can be reduced to from 6 to 8 per cent of the total alumina quantity.

Reducing the quantity of alumina to from 15 to 20 per cent has the following potential advantages:

- Improvement of the internal environment, i.e. the sulphur load is apparent in that less SO_2 is returned with the alumina. There seems to be a limit to the amount of SO_2 which the alumina can absorb. When this limit is reached, the amount of SO_2 recycled is reduced in proportion to the alumina feed. In practice, this means that when the sulphur content in the petroleum coke exceeds 2.5 to 2.7 per cent, it will be possible to capitalize on this effect to the full.

- Improvement of the internal environment, as the secondary alumina (reactor/filter catch) can be added at those times during the day/night when the opening of cover-plates and work on the pots is at a minimum. This reduces the content of dust and fluorides in the pot-room atmosphere.

- Lower investments on account of smaller capacity required for the conveyor systems and the silos for primary (fresh) and secondary alumina in the scrubbing plants and simplification of the system for distributing the alumina to the filters. This has to be weighed against the costs of the reactor and a possibly more complicated distribution system.

- Lower operation costs on account of the smaller capacity of the pneumatic conveyor system.
- Better quality metal because groups of pots can be fed with fresh alumina.
- Possibility for closed and automated pots, with their appertaining dry scrubber plants, also to be fed with secondary alumina from the Soederberg pots.
- Alumina qualities with good scrubbing properties can be reserved for dry scrubbers while larger quantities of less suitable alumina can be fed straight to the pots.

Splitting the alumina stream has the following potential advantages:

- The heavily contaminated portion can be reduced to from 6 to 3 per cent. This offers further possibilities of routing the return contaminants to a small number of pots.
- Filter catch contains all the returned Na_2O. Pots at start up have a deficit of Na_2O, while older pots have a surplus. The filter catch can, if required, be fed to newly started pots. This assumes that these pots can take the other contaminants.

6. Description of low- and non-waste processing technology

(a) Technical characteristics

When the alumina is exposed to the pot gases, there is a certain pick-up of various elements. An analysis of the alumina before and after the dry scrubbers is presented in Table 2. The quality of the metal produced with the exposed alumina shows a slightly inferior quality. This is shown in Table 3.

(b) Cost estimates of dry scrubber/reactor installations

Compared with wet scrubbing, the initial cost for a dry scrubber may appear rather high. However, when the costs of wet scrubbing with cryolite recovery and liquid effluent disposal are taken into consideration and added to the savings through the fluoride compounds being returned directly to the pots, the overall cost of installing and operating a dry scrubber is quite favourable.

Dry scrubbing pot gas from hooded prebakes

A very rough cost estimate for a dry scrubber to clean the pot gas from a smelter with an annual production of 100,000 metric tons would be in the region of NKr 50 millions. A reactor to treat flue gases from a 100,000 million tons per year aluminium smelter would cost in the region of NKr 1.3 million. It is impossible to stipulate an exact price due to individual requirements. A detailed breakdown of operating costs per year is given below:

Operating Cost	NKr x 1000 per year
Supervision and labour	1 000
Electrical power (300 kWh/t Al)	3 000
Maintenance	700
Depreciation (10% straight line)	5 000
Total operating cost:	9 700

From the above total one can deduct the credit from recovered fluorine, namely:

Pot gas concentration	70 mgF/Nm^3
Pot gas volume	1,500,000 Nm^3/h
Cleaning efficiency on total F	98%
Amount of fluorine recovered/year =.	900 tons F
Price of AlF_3 (88% pure)	NKr 3,400
Molecular weights: AlF_3(27+3x19) =	84
3F = 57	

Total credit: $900 \times \frac{84 \times 3400}{57 \times 0.88}$ = NKr 5,124,000

Net operating cost (including depreciation) .... approx. NKr 4,580,000

Dry scrubbing gas from VSS pots

ASV has for the last four years had a dry scrubber in successful operation for the cleaning of flue gasses from Vertical Stud Soederberg pots (VSS). Here about 100,000 m^3/h at NTP of gases with a concentration of about 800 to 1000 mgF/m^3 are cleaned. The flue gases were until recently passed through an electrostatic filter prior to the dry scrubber. However, now ASV has omitted the electrostatic filter and runs the flue gases directly to the dry scrubber, resulting in an exit concentration in the region of about 1 to 2 mg/Nm^3. The exposed alumina from this dry scrubber is fed to the hooded prebake pots in order not to create adverse working conditions in the Soederberg plant. The latter is, therefore, always run on fresh alumina.

Installation cost

Here again, it is difficult to give a set price, owing to the uniqueness of situations. We anticipate, however, that the cost for such an installation will be in the region of NKr 4 to 6 million. A detailed breakdown of operating costs is given below.

Operating Cost	NKr x 1000 per year
Supervision and labour	500
Electrical power (70 kWh/t Al)	350
Maintenance	160
Depreciation (10% straight line)	500
Total operating cost	1 510

From this figure may be deducted the credit from recovered fluorine, namely:

Pot gas concentration	800 mgF/Nm^3
Pot gas volume	100,000 Nm^3/h
Cleaning efficiency, total F	98%
Amount of fluorine recovered/year ..	687 tons F
Price of AlF_3 (88% pure)	NKr 3,400

Molecular weights : AlF_3 = 84

$3F$ = 57

Total credit : $687 \times \frac{84 \times 3400}{57 \times 0.88}$ = NKr 3 911 600

Net operating credit (including depreciation) approx NKr 2 400 000

9. Reporting organization

Ardal og Sunndal Verk A.S., Oslo (Norway)

10. Date of report

30 March, 1979

Table 1. Removal efficiency of pollution control equipment used in the primary aluminium industry

Equipment	Removal Efficiency Percentage		
	Solid F	Gaseous F	Total F
(a) Prebake Primary			
Fluidized bed dry scrubber	98	99	98.6
Dry electrostatic precipitator and spray tower	93	98	95.9
Multicyclone and spray tower	80	95	88.8
Cross flow dry scrubber	98	90	93.4
Multicyclone	78	-	33.6
Spray tower	80	95	88.7
Injected alumina dry scrubber	98	98	98
Chamber scrubber	85	88	86.4
Prebake Secondary (with Primary)			
Spray screen	25	80	-
Prebake Secondary (no Primary)			
Spray screen	45	93	72.1
Cross flow packed bed	84	99	92.5
(b) Vertical Soederberg Primary			
Spray tower and wet electrostatic precipitators	99	99	99
Fluidized bed dry scrubber	98	99	98.9
Dry electrostatic precipitators and spray tower	98	99	98.9
Multicyclone and venturi spray	96	99	98.8
Spray tower	75	99	93
Injected aluminium dry scrubber	98	98	98
Vertical Soederberg Secondary (with Primary)			
Spray screen	42	88	-
(c) Horizontal Soederberg Primary			
Spray screen	64	93	83
Fluidized bed wet scrubber	78	98	89.9
Spray tower and wet electrostatic precipitator	98	93	95

Table 2. Analysis of alumina quality before and after dry scrubber

Components	Before dry scrubber	After dry scrubber
Loss on ignition, %/900°C	1.0	2.5
SiO_2, %	0.024	0.030
Fe_2O_3, %	0.012	0.040
TiO_2, %	0.002	0.006
V_2O_5, %	0.004	0.015
Na_2O, %	0.60	0.70
CaO, %	0.04	0.05
ZnO, %	0.11	0.13
NiO, %	–	0.008
F, %	0.008	1.20
C, %	0.09	0.30
S, %	0.005	0.20

Table 3. Analysis of aluminium produced with 100 per cent feed of dry scrubber exposed alumina

Elements	$\Delta x = x_E - x_F$	Increase of mean guaranteed 95% less than	95% confidence interval
Fe, %	0.036	0.0412	0.036 ± 0.0064
Si, %	0.000	0.0017	0.000 ± 0.0020
Mn, ppm	2.4	3.5	2.4 ± 1.3
Ti, ppm	8.3	9.5	8.3 ± 1.5
V, ppm	43.6	47.9	43.6 ± 5.2
Cr, ppm	1.8	2.1	1.8 ± 0.3
B, ppm	0.7	1.2	0.7 ± 0.6
Zn, ppm	4.8	6.2	4.8 ± 1.7
Cu, ppm	26.7	28.4	26.7 ± 2.1
Mg, ppm	-2.6	-1.2	-2.6 ± 0.9
Ni, ppm	30.3	32.2	30.3 ± 2.3
Ga, ppm	22.7	24.8	22.7 ± 2.6
Zr, ppm	0.7	1.0	0.7 ± 0.4
Pb, ppm	21.7	23.1	21.7 ± 1.7
Sn, ppm	1.7	2.4	1.7 ± 0.8
Co, ppm	1.1	1.9	1.1 ± 0.7
Be, ppm	0.05	-	0.05 ± -

x_E = arithmetical mean of aluminium produced from exposed alumina

x_F = arithmetical mean of aluminium produced from fresh alumina

NATIONS UNIES
CONSEIL
ECONOMIQUE
ET SOCIAL

E

RESTRICTED

ENV/WP.2/5/Add.14
9 July 1981
ENGLISH ONLY

COMMISSION ÉCONOMIQUE POUR L'EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

HIGH TEMPERATURE PAN GRANULATION OF FERTILIZER MATERIALS

Transmitted by the Government of Norway

1. Identification of industry

Fertilizer industry. ISIC [1] code : 3512

2. Basic characteristics of production process

In the final step of the various fertilizer production processes the product is given a form suitable for transportation and storage as well as final application. This is accomplished by prilling or granulation of the fertilizer product.

3. Name of conventional processing technologies

Prilling and low-temperature granulation.

4. Description of conventional processing technologies

In the prilling process the concentrated solution is pumped to the top of a tower where it is sprayed downward counter-current to a stream of air which cools and solidifies the droplets. These prills are then dried further in order to reduce the moisture content to less than 0.5 per cent. Following cooling, the prills are coated with an anti-caking agent. Prilling requires large volumes of cooling air which, during its contact with the molten fertilizer material, absorbs fumes containing particles in the micron and submicron range. The amount of dust particles entrained in the cooling air ranges between 2 and 7 kg/ton of fertilizer product. The emissions from the prilling towers can be reduced by redesign of the towers or by retrofitting existing towers with scrubbers.

In the granulation process a fertilizer melt or a slurry is fed into a granulator in which feed is mixed with recycled dry fertilizer fines to form a granule. The granulated material formed in the granulator is discharged into a drier/cooler where the final product properties are defined. After the granules have solidified in the drier/cooler they are sized on vibrating screens.

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex).

GE.81-42160

In order to lower the temperature in the granulator sufficiently below the melting point of the added molten material, a large amount of cooled product material will have to be recycled. This leads to increased investments for recycling equipment.

In the drum granulators and fluidized bed granulators a considerable amount of air is brought into contact with the molten material. Although the amount of cooling air is normally less than in the prilling process, a considerable amount of fertilizer dust is emitted together with this air.

5. Name and state of development of low- and non-waste processing technology

Increased requirements with regard to both pollution control and product quality, together with a desire to lower production costs, induced Norsk Hydro to develop the "High Temperature Pan Granulation" (HTPG) technology.

After a short period of bench scale studies, a pilot plant was built in conjunction with an ammonium nitrate prilling plant at Rjukan Works where water-free ammonium nitrate melt was available. After a few months study in the pilot plant, sufficient information was available for the design of a full-scale plant. A 350 tons/day plant started up in 1971 and has been operating successfully since.

A combined AN/ANL-plant with a design capacity of 600 tons/day AN and 800 tons/day ANL is under construction in Kavalla (Greece) and a 270 tons/day urea plant is under construction for the American N-ReN Company in the Sudan.

The characteristic properties of pan granulated products are the following :

- The crushing strength is normally up to three times higher than that of prilled products.
- Due to the large flexibility in particle size, the product may be tailor made for most bulk blending purposes.
- The hardness of the material significantly reduces the tendency of dust formation during handling.
- Due to the short retention time of the hot material in the pan, undesired side-reactions are greatly suppressed. When making urea, for example, the increase in biuret from melt to final product is always less than 0.1 per cent.

6. Description of low- and non-waste processing technol

(a) Based on bench-scale experiments, a pan granulation pilot plant was erected in an existing ammonium nitrate prilling plant at Rjukan Works. The pilot plant employed water-free melt (0.5 per cent H_2O) from the evaporators and solid ammonium nitrate in the form of microprills of about 1.0 mm size. Utilizing a 0.75 m pan a spray nozzle technique and operating conditions were established which provided stable operation, high production rates and high product quality. Successful test runs with additives were performed. Quality and storage tests proved that superior resistance to mechanical and thermal stresses was obtained. The yield of granules in the desired size range proved to be so high that it was decided not to recycle the off-size from the screens in the full scale plant, but to let the small quantity dissolve to form an AN-solution

A small part of the melt from the evaporator is passed to the existing prilling tower where the prills enter the pan under weight control. This established the necessary dry feed to the pan. Figure 1 shows how this was realized when the construction of a full-size plant was executed, based on the data from the pilot plant.

In the plant, one pan of 3.5 metre diameter was installed. Production rates have been demonstrated of from 8 to 18 tons an hour. Higher loads have not been tried because of bottlenecks in other plant equipment. Today, the pan runs under automatic temperature control, utilizing the dry feed as control parameter. At fixed levels of the other pan parameters, a consistent product quality is obtained with a minimum of care. The melt/solid ratio is close to 80/20, whether the solid feed is prilled or recycled material.

The product from the pan passes through a small polishing drum where the particles attain their smooth, glossy surface.

The product coolers (rotary type) and screens are the same as used for the prilling plant and in certain periods the plant is still producing prilled products. The only new equipment installed was the two feed systems to the pan, the pan itself, the polishing drum and exhaust hoods which were arranged around the pan to protect the operators from ammonia vapours. The classifying ability of the pan is very good. The yield of product in the range 4 to 11 mm is in excess of 95 per cent. The granules have an exceptionally high crush strength, and the tamped bulk density is normally about 1 kg/litre. The water content of the product is about 0.2 per cent lower than that of the melt, because of water vaporization in the pan, leaving a product with good storage ability. No caking of the product has been reported from the field since the start of commercial production.

In the Rjukan plant, test runs were conducted to demonstrate production of normal fertilizer grades, i.e. 2 to 4 mm. For ammonium nitrate and for calcium ammonium nitrate, this was achieved by minor changes in pan parameters and in nozzle equipment and conditions. The physical properties and storage ability of the fine-grained product were as excellent as for the coarse grade product. The amount of off-size increased and recycling from the screens was established, with some addition of [illegible] balance requirements around the pan.

With no production of prills to feed the pan - and this will normally be the case - it was evident that the well-known haze (sub-micron mist) from the hot melt could easily be processed in the small amount of ventilation air from the pan hood and the nearly isothermal polishing drum. No haze is mixed into the larger amounts of air used for cooling the product, thus permitting cleaning of this air by simple mechanical means.

(b) Pan granulation of urea

After the success of the granulation technique for ammonium nitrate it was decided to explore whether or not the technique could be employed for urea to make regular size particles (2 to 4 mm) and larger particles. For this purpose a pilot plant was erected in conjunction with the urea plant at Porsgrunn Works.

The pilot plant employs urea melt directly from the plant (0.3 per cent H_2O) and uses crushed product from its own production as solid feed. The pilot plant consists of melt and solid feed systems, a pan of 0.9 metre diameter, polishing drum, drum or fluid bed cooler (either one may be used) and a screen (see Figure 2).

At the high working temperature of the pan, the agglomeration forces practically eliminate dust particles. In spite of the stickiness of the growing granules, we have had the same experience in the urea pan as is so much appreciated in the AN granulation plant : the water-free melts give very little clogging on the equipment. Simple, continuous, mechanical scrapers protect the pan bottom and rim from scale build-up, and any material scraped off will easily enter the rapid agglomeration process. Thus, there is no dust or flakes obstructing the classification in the pan. The product stream from the pan is therefore very clean. This phenomena, combined with the quick hardening of particle surfaces, prevents clogging of downstream equipment. As mentioned for ammonium nitrate, the air from the cooling section contains nothing of the sub-micron fraction, so well known from urea prilling. This appears only in the small air stream from the pan hood.

The urea pilot plant has been operated on an intermittent basis. The results obtained to date have been very good. Utilizing crushed product as solid feed to the pan, a production rate exit from the pan of 4,6 tons/m^2 hour has been obtained without any signs that the capacity limit of the pan has been reached. This rate, however, represented the limit of the feed systems to the pan. Thus, the capacity of the pan is probably significantly higher.

The classifying ability of the pan was good. The yield of particles in the range of 2 to 4 mm is about 80 per cent.

The heat of crystallization of urea is higher than that of ammonium nitrate. Thus the solid fraction of the pan must be higher in urea pan granulation. In the pilot plant a melt/solid ratio of 60/40 was observed. In a full-sized plant the melt/solid ratio will be lower because of the lower surface/volume ratio of the pan resulting in less heat loss per unit production.

Since the pilot plant utilizes crushed product as solid feed, the maximum net production demonstrated has been 4.6 x 0.6 = 2.8 tons/m^2 hr. The observed yield of 80 per cent is thus satisfactory. Actually, to satisfy the heat balance, some of the product has to be recycled to the pan, in addition to the undersized particules from the cyclone and screen and crushed oversized material, if no alternate solid feed is available. However, as a consequence of the high working temperature, the technique calls for less recycling than other processes operating at lower temperatures.

Pan granulated urea particles are rounded, but are not as spherical and glossy as pan granulated ammonium nitrate. The physical properties are very good. The particles are about three times harder than urea prills of equal size, and the tamped bulk density is high, 0.76 kg/litre. Some water is evaporated during pan granulation. The products contain about 0.1 per cent H_2O, which enhances their storage ability. The pilot plant has produced the amounts necessary to perform full scale storage tests. The products have been tested in bags (50 kg), big bags (400 kg) and in bulk piles. The different tests gave the same results. The pan granulated material was superior to prilled urea and about equivalent to prilled urea treated with surfactants. The higher particle strength of the granules resulted in less crushed material when handled in the bulk compared to prilled urea. Conditioning of pan granulated urea is therefore not required for most uses.

The biuret content of the product depends mainly on the biuret content of the melt. In the pilot plant, the increase in biuret content from melt to final product was consistently lower than 0.1 per cent.

For research on increased response to fertilization of paddy rice in flooded areas, a very coarse grade of urea is desired, so called super-granules. We have, by adjustments in our standard practice, succeeded in producing urea super granules in close-size ranges of 1, 2 or 3 grams. More than 10 tons are now shipped. To furnish research groups with increasing quantities of urea super granules, the pilot plant will now be enlarged and equipped specifically for the production of a coarse grade product.

(c) Practical process arrangement in new plants for pan granulation of ammonium nitrate or urea using the HTPG-technique

Based on the Rjukan plant experience with ammonium nitrate and the pilot plant experience with urea, the net production of one pan with a diameter of 4 metres may be estimated to be in excess of 500 tons/day. Thus, a 1000 tons/day urea plant utilizing this technique would require two 4-metre pans. The pans would require separate melt/solid feed systems, but a single train would be utilized downstream of the pans.

(d) Pan granulation of NPK

At one time, the use of coarse grade NPK as forest fertilizer was considered. A pan granulation pilot plant was installed in one of the complex fertilizer plants to study the technique in this complex multicomponent system. A pan of 0.75 m diameter was used. Compared to pan granulation of ammonium nitrate and urea, pan granulation of NPK posed some special problems. As the potassium salt (KCl or K_2SO_4) present dissolves and reacts in the water-free NP melt (mainly ammonium nitrate and ammonium phosphate), there is a pronounced and time-dependent change in the melting point of the liquid phase. Clearly, residence time in the pan and contact intensity are important factors in this process. However, when these factors are appreciated and taken into account, stable operation is obtained. Generally, the same good results as to capacity, simplicity of operation and product quality were obtained for NPK, as were obtained for ammonium nitrate and urea [1] 2/

(e) Pan granulation of nitrate of lime

Nitrate of lime is an important fertilizer in Scandinavia, and Norsk Hydro is the major producer. It has now investigated the use of the HTPG-technique to produce a coarser grade of nitrate of lime fertilizer that can be obtained by air-prilling.

Positive results have been obtained in a small pilot unit. The material was easily handled in pan and cooler. The same improvement in physical properties were observed, i.e. stronger particles and improved storage properties.

7. Schematic comparison between the conventional and the low- and non-waste technology

As described, the same pan granulation technique has been utilized for the five products investigated, e.g. ammonium nitrate, calcium ammonium nitrate, urea, NPK and nitrate of lime. The technique is distinctly different from other pan granulation techniques which are reported in patents and publications [3,4,5,6] 2/. Patents for the HTPG-technique have been granted in a number of countries, e.g. Norway, United Kingdom, India, German Democratic Republic and United states [2] and claims have been accepted and are under consideration in several other countries. A summary of the characteristic features of the technique is given below.

2/ Numerals in square brackets refer to references at end of text.

The HTPG-technique employs a pan of conventional design. The most outstanding feature of the HTPG-technique is the very high temperature of the product leaving the pan. Other pan granulation techniques for water-free melts operate at temperatures more than 40 °C below the crystallization temperature of the melt, utilizing essentially a layering method in the build up of particles. The HTPG-technique employs temperatures much closer to the crystallization point. For the products investigated, optimal temperatures of the particles leaving the pan varied from a few degrees to about 25 degrees below the crystallization point of the respective melts.

Compared to low temperature pan-granulation techniques, the HTPG-technique provides significantly higher particle-growth rates. The higher temperature also reduces the recycle requirement. The HTPG-technique thus results in a pan granulation operation with significantly higher net production rates from the pan. The pan is a cheap and highly valued piece of equipment in large-scale production of other materials (cement, clinker, minerals, ores, etc.) in pellet form. In spite of this fact, the pan is said to have too low a specific load for fertilizer use. With the HTPG-technique, the authors believe this is no longer a valid argument.

The use of pan granulation facilitates the cleaning of the cooling air compared to prilling. The air may be used more efficiently, thus reducing the total air requirement. Besides, only small amounts of air are in contact with the melt at high temperatures in the pan, as mentioned above.

The pollution control installations for the pan granulation process also avoid expensive duct work found in prilling installations, as the major plant equipment is located near ground level.

The utilities consumption for the pan granulation process are low compared to other granulation processes as no drying of the product is needed and considerably less material has to be handled due to the high granulation efficiency. Less energy is required for off-gas treatment.

Norsk Hydro has calculated the grassroots investment for a 1500 t/d granulation unit for urea, AN and ANL to be about US$ 8 million.

References

(1) T. Grundt and T. Heggebø, "The Norsk Hydro NPK Process". Paper presented at Norsk Hydro's Symposium on Fertilizer Technology (Czechoslovakia), October, 1978.

(2) Ø. Skauli, Norway, agent to Norsk Hydro, A.S., U.S. Patent no. 4 068 064, 15 February, 1977.

(3) J.B. Thompson and G.C. Hildred, agents to Cominco Ltd., U.S. Patent 3 408 169, 29 October, 1968.

(4) R.D. Young and I.W. McCamy, TVA, Muscle Shoals, Alabama (USA), TVA Development Work and Experience with Pan Granulation of Fertilizers. The Canadian Journal of Chemical Engineering . Vol. 45 : 50-56, February 1967.

(5) R.S. Meline, I.W. McCamy, J.L. Graham and T.S. Sloan : Plant-Scale Granulation of Fertilizers in a Pan Granulator. Journal of Agricultural and Food Chemistry, Vol. 16, 235-240, March/April 1968.

(6) T. Fabris, T. Borelli, C. Schiavello and O. Bagnati (Italy), agents to Montecatini Societa Generale per l'Industria Mineraria e Chimica, Milan, Italy. US Patent 3 117 020. 7 January,1964

FIGURE 1

AMMONIUM NITRATE PAN GRANULATION
PRODUCTION OF COARSE GRADE FOREST FERTILIZER
AT RJUKAN WORKS
PROCESS ARRANGEMENT
NEW EQUIPMENT SHOWN IN GRAY

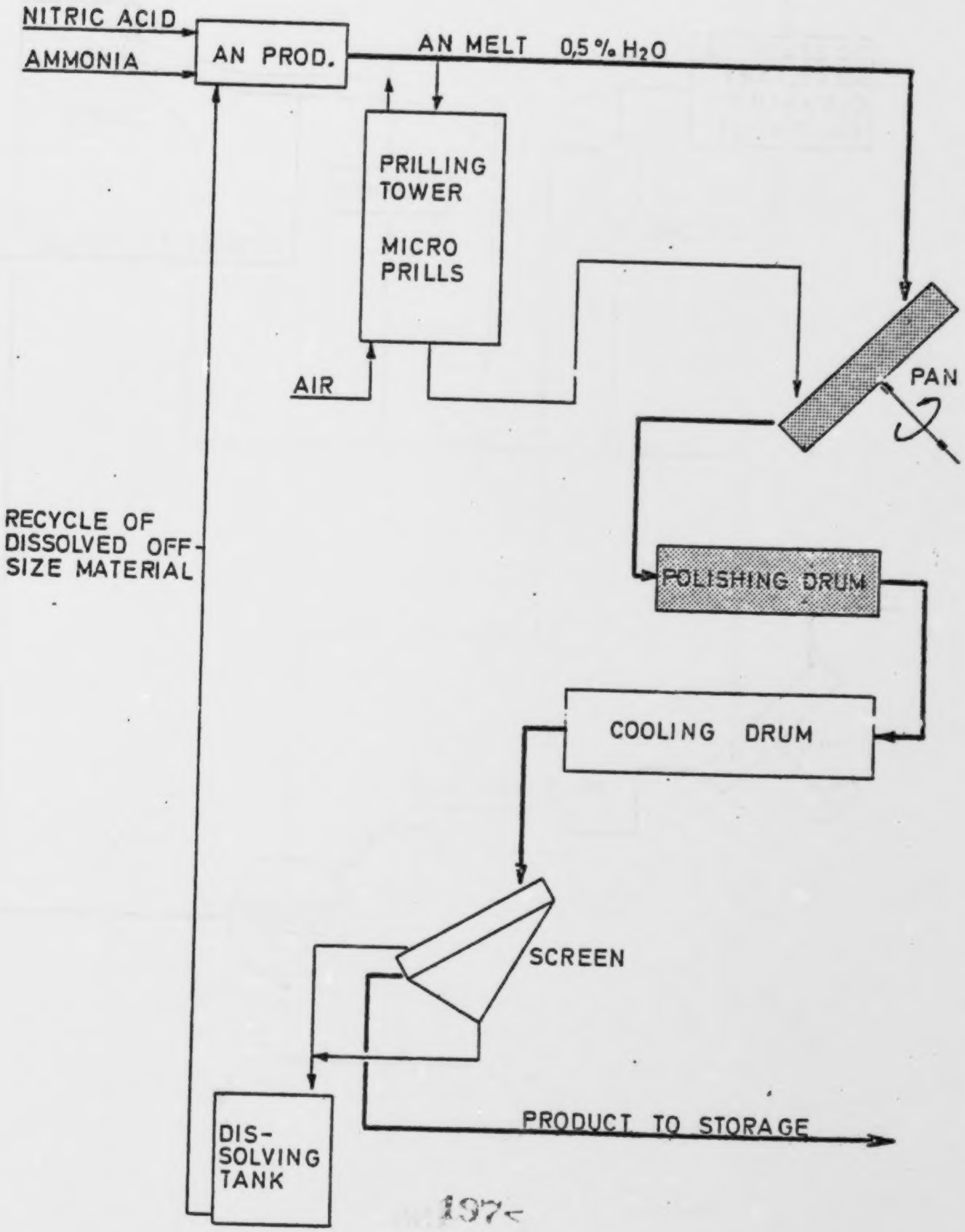
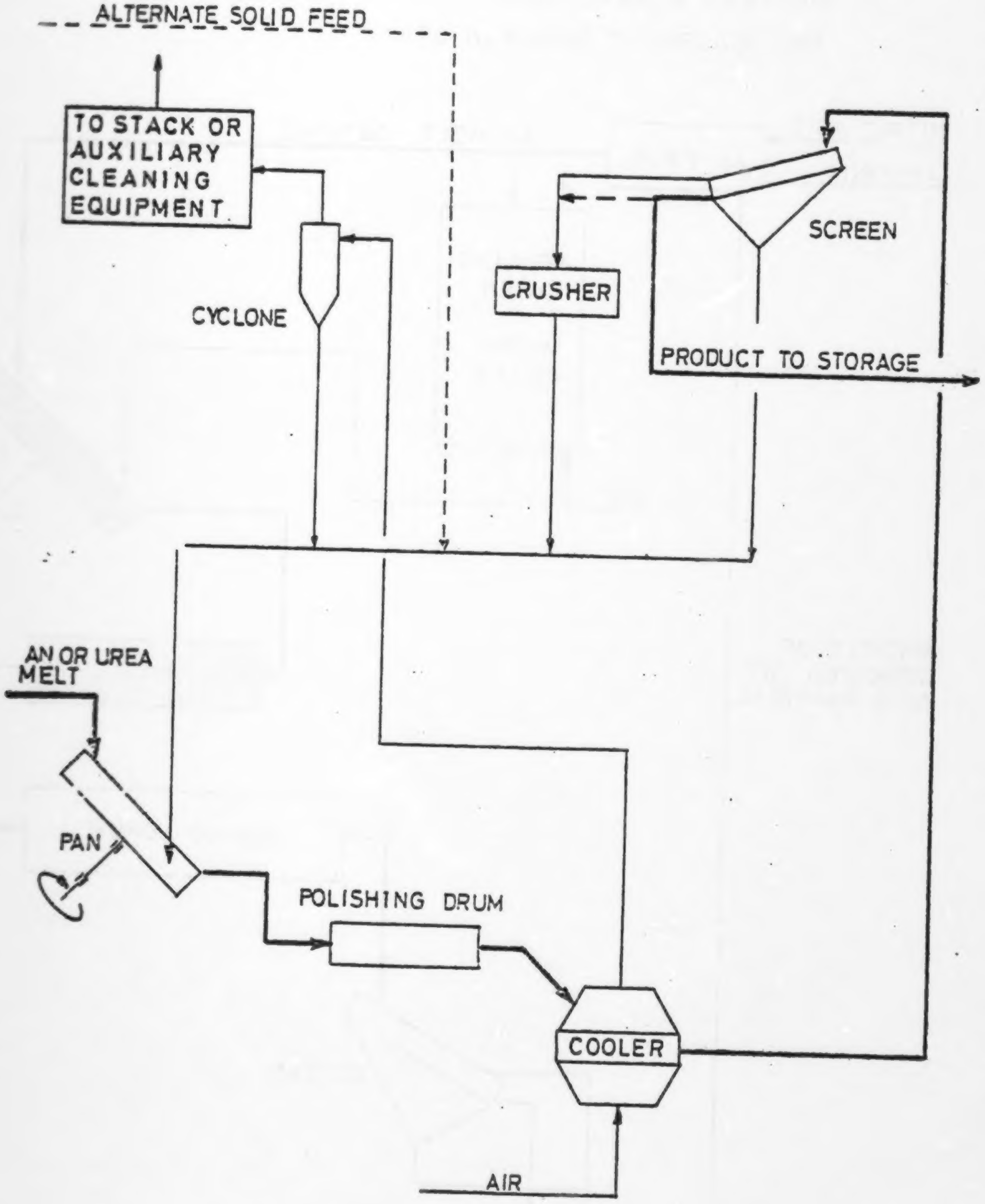

NITRIC ACID
AMMONIA
AN PROD.
AN MELT 0,5 % H₂O
PRILLING TOWER
MICRO PRILLS
AIR
PAN
RECYCLE OF DISSOLVED OFF-SIZE MATERIAL
POLISHING DRUM
COOLING DRUM
SCREEN
DIS-SOLVING TANK
PRODUCT TO STORAGE

FIGURE 2

AMMONIUM NITRATE OR UREA PAN GRANULATION

PROCESS ARRANGEMENT IN A NEW PLANT


ALTERNATE SOLID FEED
TO STACK OR AUXILIARY CLEANING EQUIPMENT
CYCLONE
CRUSHER
SCREEN
PRODUCT TO STORAGE
AN OR UREA MELT
PAN
POLISHING DRUM
COOLER
AIR

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

RESTRICTED

ENV/WP.2/5/Add.15
July 1981
ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE
SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

PREPARATION OF MOULDING SANDS CONTAINING RECLAIMED SANDS

Transmitted by the Government of Poland

1. Identification of industry

Foundry practice. ISIC [1] code: 3710

2. Basic characteristics of the production process

Speaking in general terms, the current methods of making castings in sand moulds consist of pouring moulten metal into a foundry mould; a special moulding box is used and, after the solidification of metal in the mould, the used moulding sand and the casting is knocked out of the box. Sands used for foundry moulds contain about 90 per cent silica sand, which constitutes 50 per cent of the total cost of all the sand components.

The high cost of the new sand (including its transport and preparation), as well as the difficulties and expenses resulting from handling the used sand, make it absolutely necessary to increase the recovery rate of foundry sands. Recently, this problem has become particularly important, especially in view of the growing production and mechanization; this is especially true with the introduction of modern mould- and core-making technologies using self-hardening and chemo-setting sand mixtures (where the sand must be subjected to a special recovery treatment), bringing about the ever-increasing use of new sand, with the simultaneous disposal of greater and greater amounts of used sand to the dump site.

3. Name of conventional processing technology

Preparation of moulding sands with processing of the used sand (bentonite sands only) or with a single recirculation of the sand (self-hardening sands only).

It should be emphasized here that processing of the used sand is applied only if conventional (bentonite or clay-bonded) sands prevail

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex)

in a given foundry. In the case of self-hardening and chemo-setting sands, sand-processing, in the usual sense of the word, is not sufficient, and the knocked-out sand cannot be reused.

4. Description of conventional processing technology

4.1 Description of the main operations

In discussing the conventional technology of the sand circulation system in foundries, two cases should be distinguished, namely:

(a) Bentonite (clay-bonded) sands

A flow diagram for the case where conventional sands prevail is given in Fig.1. It shows that a part of the knocked-out sand is re-used as a return sand (after rebonding it with some additions of new sand). Another part of the sand is disposed of at the dump site.

(b) Self-hardening or chemo-setting sands

A flow diagram for this type of sand, when no reclamation is applied, appears in Fig.2. The process takes the course as shown in the diagram; in practice, the total amount of the material is transported, dried, cooled and, after having been knocked out, disposed of at the dump site. It is clear that in both cases, large amounts of sand are disposed of at the dump site after one single use and new sand is introduced to replace the old. Obviously, this new sand must have preciously been prepared, which, in turn, results in the consumption of energy and some definite capital outlays.

4.2 Specification of materials and energy requirements per ton of castings

First of all, it should be made clear that the amount of moulding sand used in a production cycle exceeds by several, and sometimes even by several dozen, times the mass of the castings actually produced.

In addition, if one were to calculate that when the conventional sands are processed (in which case the factor $m = \frac{\text{weight of moulding sand}}{\text{weight of casting}}$ reaches the value of 20 per cent in the case of automatic moulding lines), the theoretical sand recovery rate amounts to 90 per cent, while in practice it oscillates at a level of 50 to 60 per cent. One may then adopt, for further discussion and comparisons, the following extreme values:

A. For bentonite (clay-bonded) sands

Factor $m = \frac{\text{moulding sand weight}}{\text{casting weight}}$	5		20	
Sand recovery rate from used sand processing	50%	90%	50%	90%
Sand consumption rate per 1 t of castings	2.5 t	0.5 t	10 t	2 t
Energy consumption rate per 1 t of castings	1500 MJ	300 MJ	6000 MJ	1200 MJ

B. For self-hardening or chemo-setting sands (without reclamation)

Factor $m_{average} = \frac{\text{moulding sand weight}}{\text{casting weight}}$	5
Sand consumption rate per 1 t of castings	5 t/t
Energy consumption rate per 1 t of castings	3000 MJ

4.3 Generation of waste

The waste materials disposed of at the dump site (used moulding sand) are of a different chemical composition, depending on the type of the technological process applited in a given foundry shop, and of a highly varied grain size, ranging from fine dust up to large lumps.

On fact should be noted here: although these are solid waste materials, they are a serious threat to both groundwater (danger of contamination with the substances washed out of the knocked-out sand by rainwater) and to the atmosphere (danger of the dust being spread by the wind).

4.4 Specification of the emission/effluent/solid waste standards applicable in the reporting country or area

Not reported

4.5 Problems of environmental pollution control

Control of the degree of environmental pollution, when disposing of the used moulding sand, consists mainly of the evaluation of the type and amount of harmful or toxic substances which may be washed out of the sand when it is "rinsed" with rainwater.

4.6 Specification of the waste emitted to the environment

The amount of solid waste disposed of at dump sites in the form of knocked-out sand, calculated in respect to the sand recovery factor and the sand consumption factor m discussed previously, is given below:

A. For bentonite (clay-bonded) sands

Factor m	5		20	
Sand recovery rate from used sand processing	50%	90%	50%	90%
Disposal of used moulding sand per 1 t of castings	2.5 t	0.5 t	10 t	2 t

B. For self-hardening or chemo-setting sands (without reclamation)

Factor $m_{average}$	5
Emission of used moulding sand per 1 t of castings	5 t

5. Name and state of development of low- and non-waste processing technology

Preparation of moulding sands with reclaimed sand (for bentonite sands, both sand processing and reclamation; for self-hardening sands, reclamation only).

Sand processing has been known for a long time, and it has been introduced into a number of foundries which use mostly bentonite (clay-bonded) sands.

In Poland, after laboratory, semi-technical and industrial tests, sand reclamation has been introduced into 10 foundries. Attempts aiming at a practical implementation of this method have already been made in several domestic foundries.

6. Description of low- and non-waste processing technology

6.1 Main operations

In the case of both bentonite (clay-bonded) sands.- when sand processing is applied - and self-hardening or chemo-setting sands, an increase in the sand recovery rate can be obtained by reclaiming that part of the material which had formerly been discharged to the dump site. A flow diagram for bentonite sands and the low-waste technology is shown in **Fig.3**. Attention should be paid to the fact that the product, which is recovered from the knocked-out sand from the processing plant, is the moulding mixture, while the product obtained from the reclamation process is the recovered sand.

Flow diagrams for the bentonite (clay-bonded) sands and the self-hardening or chemo-setting sands, when the low-waste technology is applied, are shown in Figs. 3 and 4.

A mere comparison of these systems with the conventional ones (shown in Figs. 1 and 2) points to the fact that with an application of the low-waste technology, the amount of recovered sand rapidly increases, while the amount of waste materials to be disposed of is considerably reduced.

6.2 Specification of materials and energy requirements

In Poland, in the dry reclamation process, the sand-recovery rate amounts at present to about 70 to 85 per cent. Adopting for further discussion the lower value of 70 per cent, and using the data given under item 4.2, the following values of the materials and energy requirements can be specified in the case of the low-waste technology:

A. For bentonite (clay-bonded) sands

	Factor $m = \frac{\text{moulding sand weight}}{\text{casting weight}}$			
	5		20	
Sand recovery rate from sand processing	50%	90%	50%	90%
Synthetic factor of sand recovery from sand processing and reclamation	85%	97%	85%	97%
New sand consumption rate per 1 t of castings	0.75	0.15	3	0.6
Energy consumption rate per 1 t of castings	450 MJ	90MJ	1800 MJ	300 MJ

B. For self-hardening or chemo-setting sands

Factor $m_{average} = \frac{\text{moulding sand weight}}{\text{casting weight}}$	5
New sand consumption rate per 1 t of castings	1.5
Energy consumption rate per 1 t of castings	900 MJ

6.3 Generation of wastes

When the sand is reclaimed, the type and amount of waste materials are changed. Now, the waste will mainly consist of:

- dusts arising from sand processing and reclamation;
- rejects such as lumps and agglomerates from the processing and reclamation plants;
- a certain amount of knocked-out sand which for some reason was not handled in either the processing or the reclamation plant.

If the sand is reclaimed, given the sand recovery and consumption factors discussed previously, the amount of solid waste disposed of at the dump site from the processing and reclamation plants and partly from the knocked out sand will assume the following values:

A. For bentonite (clay-bonded) sands

Factor m	5		20	
Sand recovery rate from used sand processing	50%	90%	50%	90%
Total sand recovery rate from sand processing and reclamation	85%	97%	85%	97%
Solid waste disposal rate per 1 t of castings	0.75 t	0.15 t	3 t	0.6 t

B. For self-hardening or chemo-setting sands

Factor $m_{average}$	5 t
Sand recovery rate from reclamation	70%
Solid waste disposal per 1 t of casings	1.5 t

7. Comparison between the conventional and the low- and non-waste technology

Flow diagrams which apply to the conventional and low-waste technologies for moulding sands used in the foundries are shown in Figs 5 and 6 in Tables 1 and 2, methods of calculating some chosen unit cost items for the moulding sand in both variants are indicated, together with a comparison of the main characteristics of these variants.

7.1 Materials and energy requirements

By application of the low-waste technology, it is possible to reduce the unit silica sand consumption rate, obtaining the following values:

- in the case of bentonite (clay-bonded) sands - at least by approximately 0.35 t/1 t of castings with m=5, and at least by approximately 1.4 t/1 t of castings with m=20;
- in the case of self-hardening or chemo-setting sands - by approximately 3.5 t/1 t of castings.

At the same time, due to the fact that considerably less sand has to be handled and dried, and the amount of the knocked-out sand to be disposed of also diminishes, the rate of fuel and energy consumption may also be reduced, as follows:

- in the case of bentonite (clay-bonded) sands reduced by, at least, about 210 MJ/1t of castings with m=5, and by at least about 840 MJ with m=20;

- in the case of self-hardening or chemo-setting sands reduced by about 2,100 MJ/1t of castings.

7.2 Generation of wastes

The application of this low-waste technology reduces the amount of waste material to the same degree to which the amount of new sand being used is reduced. The waste materials generated are of the same type (solid waste) as is the case for conventional technology.

Certain variations in the grain size of the waste are evident, namely the content of dusts is higher. It should be underlined, however, that dusts can be utilized, e.g. in the production of building elements.

7.3 Environmental pollution control measures

When replacing the convent ional technology by the low-waste technology, no new measures for the control of environmental pollution are required.

7.4 Problems of the discharge of pollutants to the environment

In view of a considerable reduction in the amount of waste when using a low-waste technology, the problem of the discharge of pollutants to the evironment is much easier to control. All the possible means of protection and preventive action are the same as those applied in the conventional technologies. However, the amount of the material treated is much smaller.

7.5 Investment requirements and unit costs

In the implementation of the sand reclamation process, no special investment outlays are required in plants where foundry machines are produced. Investment outlays are necessary in foundries where reclamation is actually introduced.

It is obvious that both the investment costs for the installation of a reclamation plant and the unit costs of production will depend, first of all, on the amount of sand reclaimed and on the capacity of the reclamation plant installed.

In Poland, the following cost figures have been recorded this year:

- cost of 1 ton of new sand (sand price + cost of drying)		350zl
- installation for dry mechanical reclamation of a capacity Q = 10 t/h		
- cost of reclamation unit		20 Mzl
- cost of 1 ton of reclaimed silica sand	about	70zl
- installation for dry mechanical reclamation of a capacity Q = 4 t/h		
- cost of reclamation unit	about	8 Mzl
- cost of 1 ton of reclaimed silica sand	about	30zl

7.6 Other differences between the conventional and the low-waste technology

One of the main differences is the fact that the use of reclaimed sand is advisable also from the purely technological point of view. Due to the thermal effect (flow of heat from the molten metal), some of the sand grains undergo important polymorphic transformations which result in dimensional changes. The reclaimed sand is thus characterized by a lower coefficient of expansion, compared with new sand. Therefore, the moulding mixture, which is prepared with reclaimed sand, reveals less tendency towards the problems which are due to expansion.

8. Identification of needs for further research and development with regard to the low and non-waste technology

The need for further research in this field arises from the fact that new types of moulding sands with organic and inorganic binders are being introduced into the foundry practice. As a rule, tests should be carried out in each case to determine a maximum possible content of reclaimed sand in the newly prepared moulding sand mixture. Apart from this, the installations for sand reclamation should be improved continually, and this can be expected to bring about a reduction in their overall dimensions, and in the unit costs. Improvements in the installations should also provide further refinement in the quality of reclaimed sands thus obtained.

9. Reporting organization

Foundry Research Institute
Zakopiańska 73
30-418 Kraków, Poland,
Dr. Eng. Andrzej Pajak

10. Date of report

9 November, 1979.

Table 1 - Example of comparison of the cost of particular components of a moulding sand (cost unit/1 ton of castings) and its variation after the application of a reclamation process

For conventional technologies

A. for bentonite sands (90% sand recovery from processing)

	factor m = 5	factor m = 20
new sand	175	700
sand drying and cooling	34	132
disposal of waste to dump site	12.5	50
Total	221.5 zl	882 zl

B. for self-hardening or chemo-setting sands

new sand	1400
sand drying and cooling	340
disposal of waste to dump site	125
Total	1865 zl

For LWT technologies (using 70% of recovered sand from reclamation)

A. for bentonite sands (90% sand recovery from processing)

	factor m = 5	factor m = 20
new sand	52.5	210.0
sand drying and cooling	10.2	40.8
disposal of waste to dump site	3.75	15.0
sand reclamation	36.0	144.0
Total	102.45 zl	409.8 zl

B. for self-hardening or chemo-setting sands

new sand	525
sand drying and cooling	102
disposal of waste to dump site	37.5
sand reclamation/amortization + operating costs	252.0
Total	916.5 zl

Table 2

Comparison between conventional technology and low-waste technology

Item compared	Production parameters	Conventional technology	Low-waste technology	Difference
MATERIAL new sand consumption per 1t of castings	A. bentonite sands			
	m = 5 u_{sp} = 50%	2,5 t	0,75 t	1.75 t
	m = 5 u_{sp} = 90%	0,5 t	0,15 t	0.35 t
	m = 20 u_{sp} = 50%	10,0 t	3.0 t	7,0 t
	m = 20 u_{sp} = 90%	2.0 t	0,6 t	1.4 t
	B. self-hardening sands	5.0 t	1,5 t	3.5 t
ENERGY energy consumption per 1t of castings	A. bentonite sands			
	m = 5 u_{sp} = 50%	1500 MJ	450 MJ	1050 MJ
	m = 5 u_{sp} = 90%	300 MJ	90 MJ	210 MJ
	m = 20 u_{sp} = 50%	6000 MJ	1000 MJ	4200 MJ
	m = 20 u_{sp} = 90%	1200 MJ	360 MJ	940 MJ
	B. self-hardening sands	3000 MJ	900 MJ	2100 MJ
EMISSION OF WASTE per 1t of castings	A. bentonite sands			
	m = 5 u_{sp} = 50%	2,5 t	0.75 t	1,75 t
	m = 5 u_{sp} = 90%	0,5 t	0,15 t	0.35 t
	m = 20 u_{sp} = 50%	10,0 t	3.0 t	7.0 t
	m = 20 u_{sp} = 90%	2.0 t	0,6 t	1.4 t
	B. self-hardening sands	5.0 t	1,5 t	3.5 t
Type of emitted waste	bentonite and self-hardening sands	knocked-out sand	knocked-out sand and rejects from reclamation plant	not significant
Investment outlays for installation	capacity			
	Q = 4 t/h	-	8 mln zl	8 mln zl
	Q = 10 t/h	-	20 mln zl	20 mln zl
Unit cost of some moulding sand components in relation to 1t of castings	A. bentonite sand			
	m = 5 u_{sp} = 90%	221 zl	102,45 zl	110.55 zl
	m = 20 u_{sp} = 90%	882 zl	400,80 zl	472,20 zl
	B. self-hardening sands	1865 zl	916.50 zl	948.50 zl

Factor $m = \frac{\text{moulding sand weight}}{\text{casting weight}}$

u_{sp} = sand recovery rate due to used sand processing

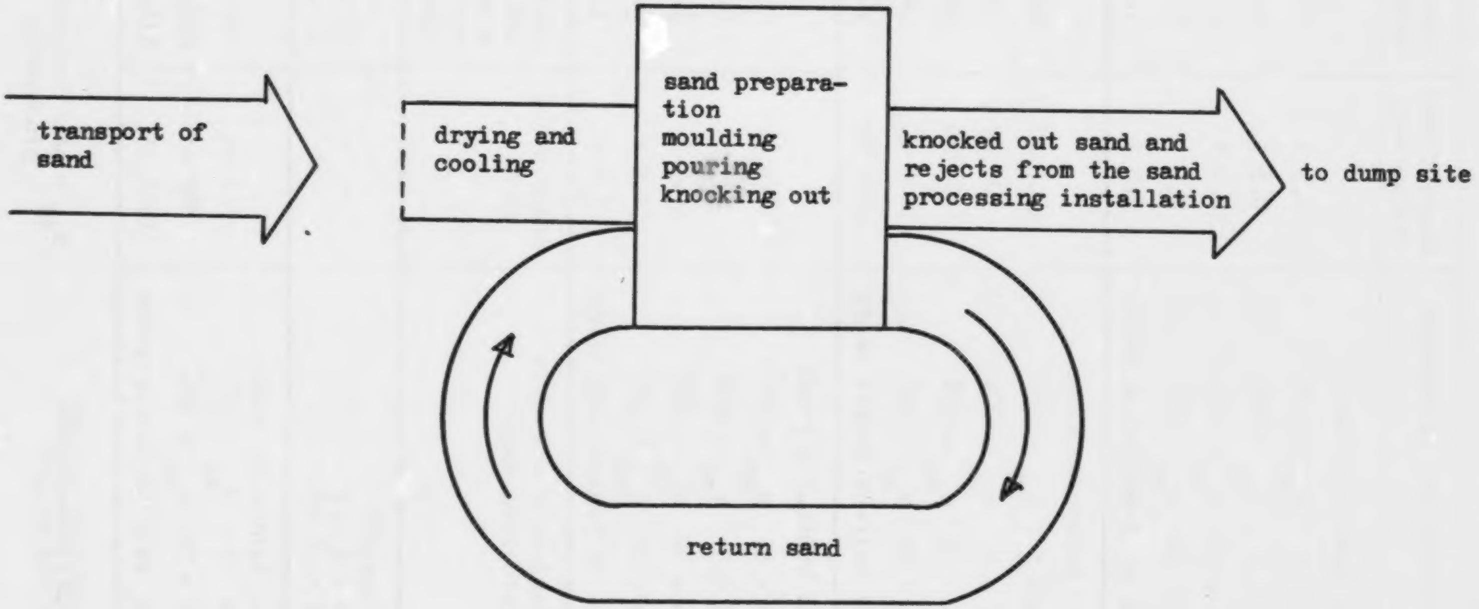

transport of sand
drying and cooling
sand preparation
moulding
pouring
knocking out
knocked out sand and rejects from the sand processing installation
to dump site
return sand

Fig. 1 - Sand recovery from processing of return sand - this refers only to the case where traditional sands prevail

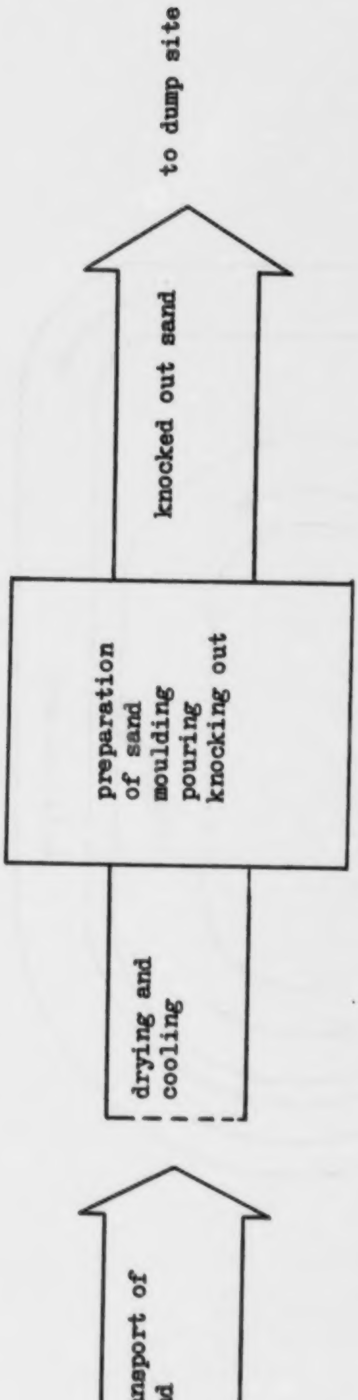

transport of sand
drying and cooling
preparation of sand
moulding
pouring
knocking out
knocked out sand
to dump site

Fig. 2 - Recirculation of sand without recovery

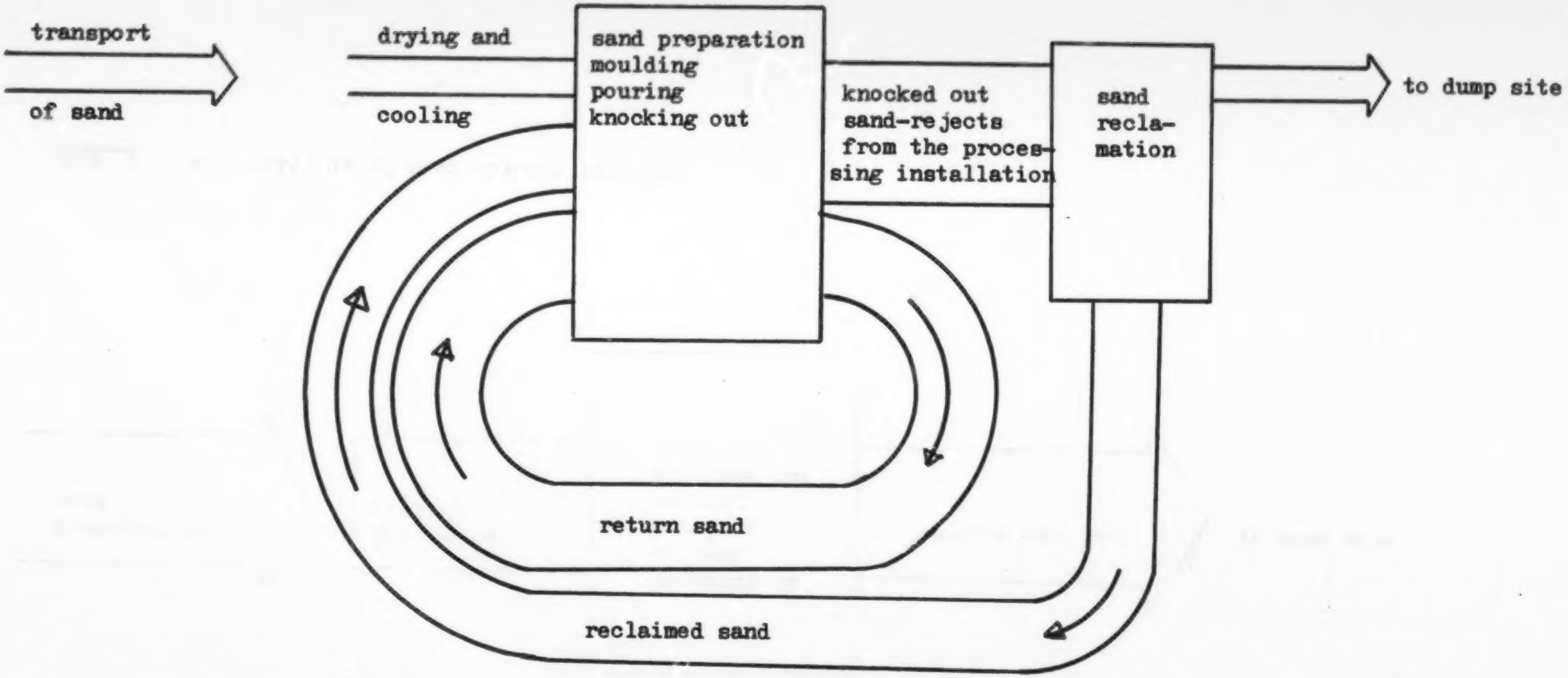

transport
of sand
drying and
cooling
sand preparation
moulding
pouring
knocking out
knocked out
sand-rejects
from the processing installation
sand
reclamation
to dump site
return sand
reclaimed sand

Fig. 3 - Sand recovery from processing of return sand and reclamation - this refers to the case when only traditional sands are used or a combination of the traditional and self-hardening sands

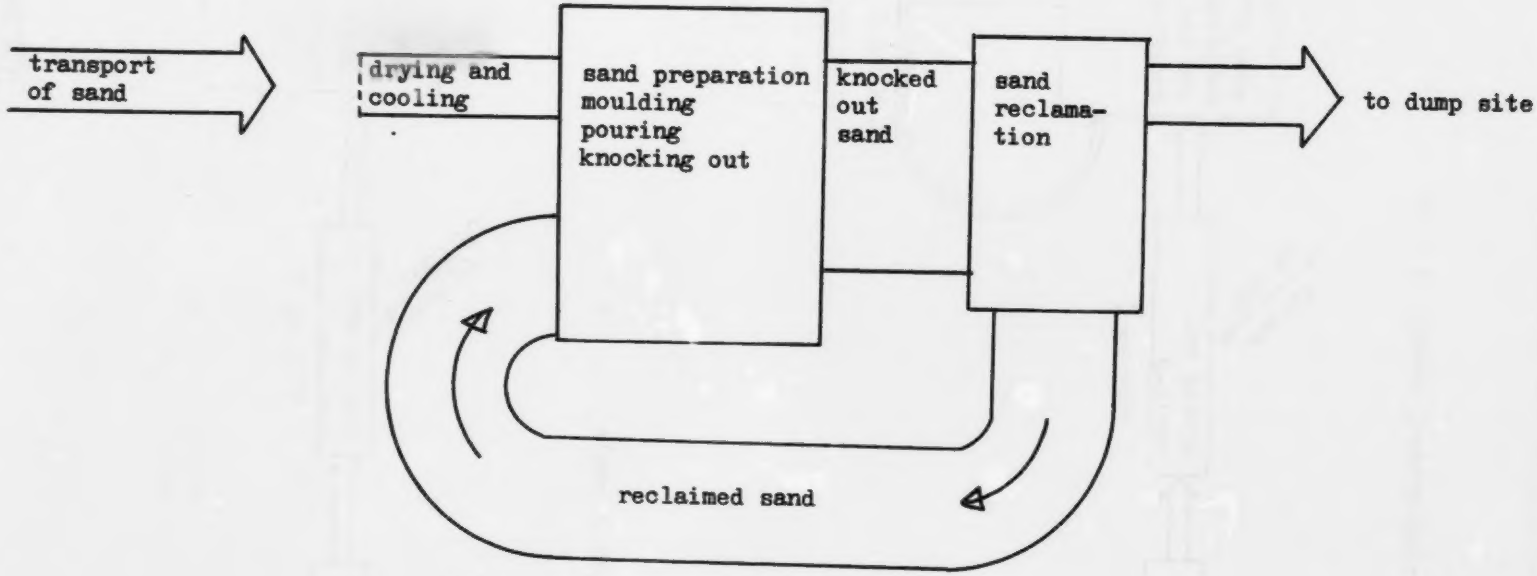
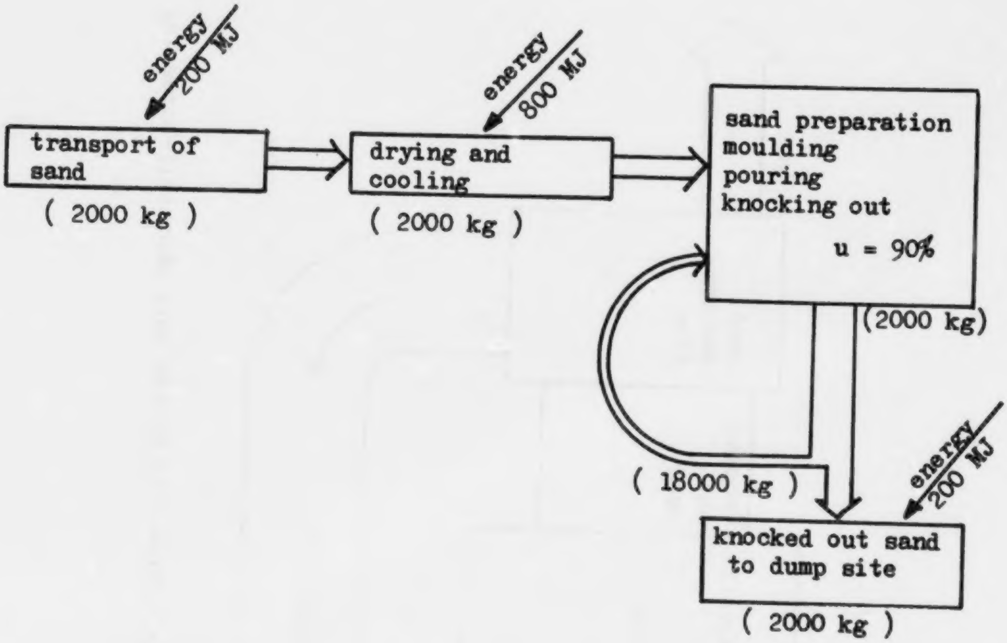

transport of sand
drying and cooling
sand preparation
moulding
pouring
knocking out
knocked out sand
sand reclamation
to dump site
reclaimed sand

Fig. 4 - Sand recovery from reclamation process - this refers only to the case when self-hardening sands prevail

FIG. 5 EXAMPLE OF FLOW DIAGRAM FOR CONVENTIONAL SAND SYSTEM

A. for bentonite (clay-bonded) sands; m = 20


energy 200 MJ
energy 800 MJ
transport of sand
(2000 kg)
drying and cooling
(2000 kg)
sand preparation
moulding
pouring
knocking out
u = 90%
(2000 kg)
(18000 kg)
energy 200 MJ
knocked out sand to dump site
(2000 kg)

B. for self-hardening sands m = 5

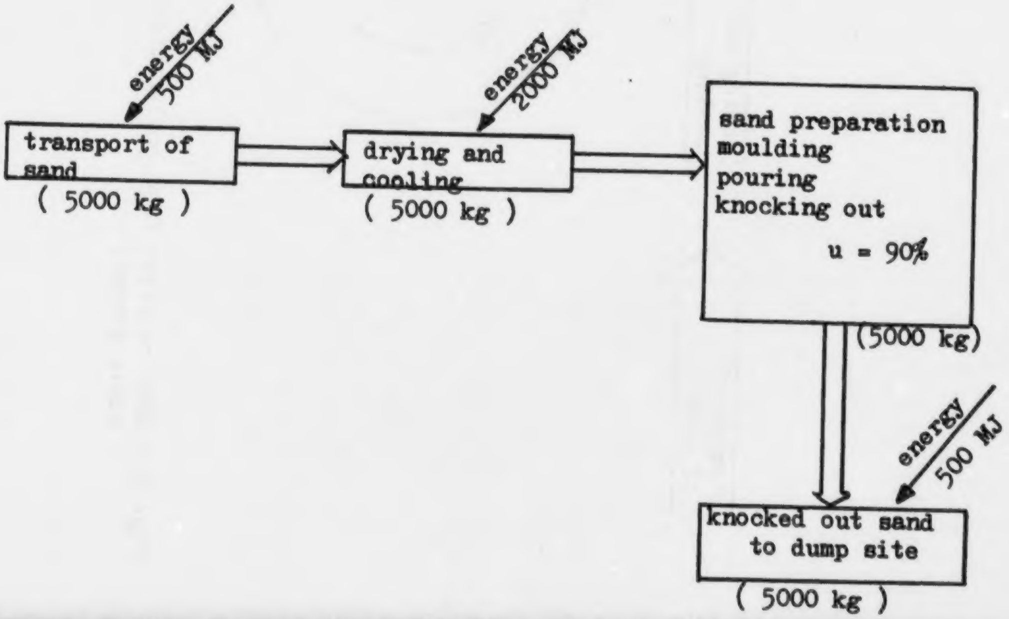
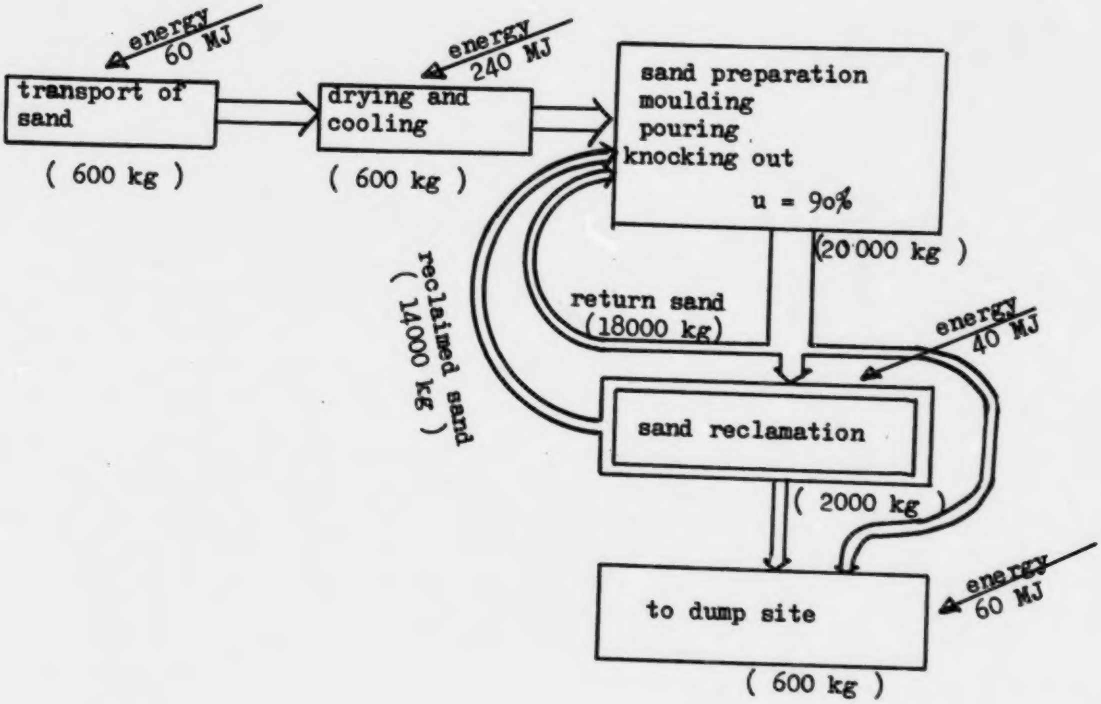
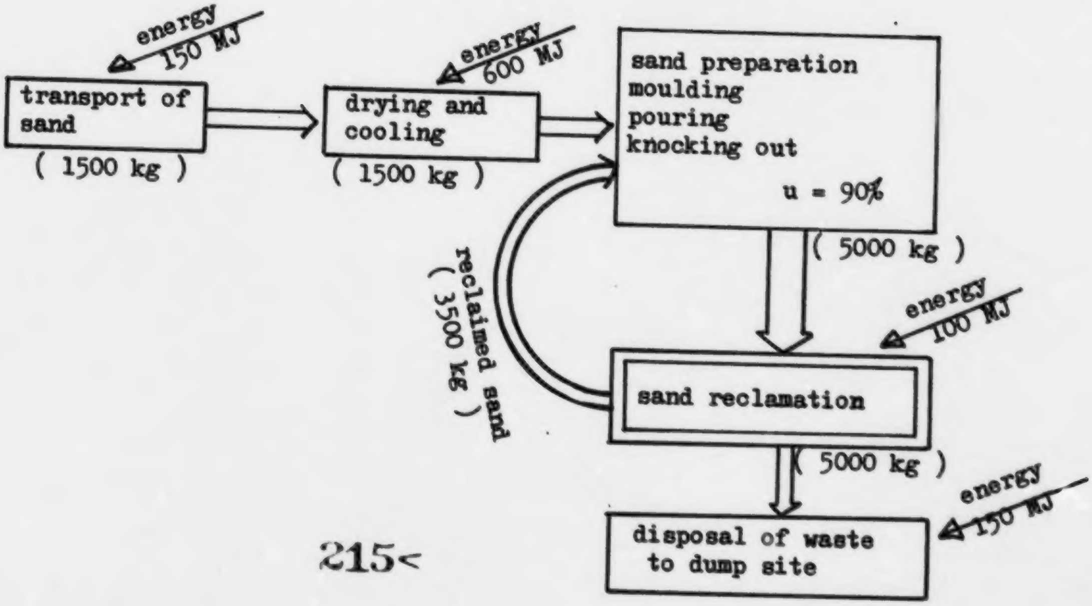

energy 500 MJ
energy 2000 MJ
transport of sand
(5000 kg)
drying and cooling
(5000 kg)
sand preparation
moulding
pouring
knocking out
u = 90%
(5000 kg)
energy 500 MJ
knocked out sand to dump site
(5000 kg)

FIG. 6 EXAMPLE OF FLOW DIAGRAM OF SAND USING RECLAMATION (LOW-WASTE TECHNOLOGY)

A. for bentonite (clay-bonded) sands ; m = 20


energy
60 MJ
transport of sand
(600 kg)
energy
240 MJ
drying and cooling
(600 kg)
sand preparation
moulding
pouring
knocking out
u = 90%
(20 000 kg)
return sand
(18000 kg)
reclaimed sand
(14000 kg)
energy
40 MJ
sand reclamation
(2000 kg)
to dump site
energy
60 MJ
(600 kg)

B. for self-hardening sands m = 5


energy
150 MJ
transport of sand
(1500 kg)
energy
600 MJ
drying and cooling
(1500 kg)
sand preparation
moulding
pouring
knocking out
u = 90%
(5000 kg)
reclaimed sand
(3500 kg)
energy
100 MJ
sand reclamation
(5000 kg)
energy
150 MJ
disposal of waste
to dump site

ОБЪЕДИНЕННЫЕ НАЦИИ
ЭКОНОМИЧЕСКИЙ
И СОЦИАЛЬНЫЙ СОВЕТ

RESTRICTED
ENV/WP.2/5/Add.16
9 June 1981
RUSSIAN ONLY

ЕВРОПЕЙСКАЯ ЭКОНОМИЧЕСКАЯ КОМИССИЯ

СТАРШИЕ СОВЕТНИКИ ПРАВИТЕЛЬСТВ СТРАН ЕЭК
ПО ПРОБЛЕМАМ ОКРУЖАЮЩЕЙ СРЕДЫ

Рабочая группа по малоотходной и безотходной
технологии и использованию отходов

КРАТКОЕ РУКОВОДСТВО ПО МАЛООТХОДНОЙ И БЕЗОТХОДНОЙ ТЕХНОЛОГИИ

Монография

ТЕХНОЛОГИЯ КОМПЛЕКСНОГО ПРОИЗВОДСТВА ГЛИНОЗЕМА И ЦЕМЕНТА

Передано правительством Польши

1. ОТРАСЛЬ ПРОМЫШЛЕННОСТИ 3699

2. ОСНОВНЫЕ ДАННЫЕ, ХАРАКТЕРИЗУЮЩИЕ МЕТОД ПРОИЗВОДСТВА

Основным сырьем, применяемым в спеково-распадовом методе Е. Гжимека, являются глины с содержанием не менее 30% Al_2O_3 и весовым отношением $SiO_2:Al_2O_3$ не выше 2 и весовой пропорцией $Al_2O_3:Fe_2O_3$ не меньше 5, и известняк с содержанием около 55% CaO.. Размолотое и уединенное глинистое сырье и известняк обжигают на спек в цементнообжигательных печах в температуре ок. 1300°C. Охлажденный спек в результате полиморфической перемены $\beta \to \gamma$ Ca_2O_4 разлагается в мелкую пыль специфической поверхностью около 10000 $см^2/г$. Полученную пыль выщелачивают 5% водным раствором Na_2CO_3. Фильтрат алюмината натрия обескремнивают, карбонизуют и кальцинируют. Остаток после выщелачивания и фильтрации является ценным материалом для получения портланд-цементов. Глинозем, полученный спеково-распадовым методом Е. Гжимека, характеризуется высокой чистотой и хорошим качеством для производства металлического алюминия.

3. НАИМЕНОВАНИЕ ТРАДИЦИОННОЙ ТЕХНОЛОГИИ

Производство глинозема методом Баера

4. ОПИСАНИЕ ТЕХНОЛОГИЧЕСКОГО ПРОЦЕССА ПО ТРАДИЦИОННОМУ МЕТОДУ БАЕРА

Метод Баера пригоден лишь только для переработки бокситов с ограниченным содержанием кремнезема (ок. 5%) Производство этим методом глинозема из сырья со значительным содержанием SiO_2 неэкономично из-за значительных потерь глинозема и щелочей в отходном осадке.

Получение глинозема по методу Баера заключается в растворении под давлением в автоклавах гидроокисей алюминия, содержащихся в размолотых бокситах, в 90% растворе едкого натрия и образования метаалюмината натрия $NaAlO_2$. Другие компоненты бокситов (Fe_2O_3 и TiO_2 и частично кремнезем) не растворяются в растворе едкого натрия и остаются в осадке. Шликер разбавляют и после разделения осадка, именуемого красным шламом, промывают водой. Из чистого раствора алюмината натрия выделяют еще раз гидроокись алюминия. Выделенный осадок $Al(OH)_3$ промывают, кальцинируют и получают глинозем.

Reproduced from best available copy.

4.1 Отдельные операции технологического процесса (схема - рис. 1)

Производство глинозема по методу Баера охватывает следующие основные операции: дробление и размол бокситов (1). Раздробленный боксит молотят в шаровых мельницах (2) с добавлением раствора NaOH , так что выщелачивание начинается во время размола. В зависимости от химического состава и свойств боксита, его подготовка к выщелачиванию может охватывать и другие операции как усреднение, обогащение, сушку и обжигание.

Выщелачивание (3) - основой выщелачивания, подготовленных надлежащим образом бокситов, а также разложения раствора алюмината натрия является реакция:

$$Al_2O_3 \cdot H_2O + 3NaOH \rightleftarrows 2Na\,AlO_2 + (n + I)H_2O$$

Полученный шлам температурой около 70°C подогревается до ок. 100°C и сохраняют такую температуру 8-10 часов, с целью выделения содержащегося в бокситах кремнезема. Затем шлам перекачивается через несколько степеней подогревателей в автоклавы. В подогревателях температура повышается до 185°C, а в автоклавах до около 230°C, а даже и до 400°C (подогрев производится свежим паром под давлением 40 атм, а в последнее время даже 100 атм). Время пребывания шлама в автоклавах - в зависимости от температуры - 1-3 часов. Выщелачивание производится в непрерывном процессе. Из крайнего автоклава шлам проходит в батарею камер самоиспарения, в которых давление постепенно уменьшается и выравнивается с атмосферным.

Разбавление шликера (14) - из крайней камеры самоиспарения шлам подают в разбавительный аппарат, куда подводится раствор из промывки красного шлама (5). Масса из разбавительного аппарата непрерывно подается в сгуститель Дора, в котором осадок (шлам) отделяется от раствора.

Сгущение шлама (5) - после разбавления массу подают в аппарат Дора, в котором красный шлам отделяется от раствора.

Промывка красного шлама (6) - производится в батареи сгустителей ДОРА, горячей водой в системе противотока. Промытый шлам направляется на отвал, а раствор в разбавительный аппарат.

Фильтрация (7) - раствор $NaAlO_2$ из аппарата Дора направляют на контрольную фильтрацию и охлаждают в теплообменнике до ок. 60°C и смешивают с веществом зарождения цепи ("прививка").

Разлагание $NaAlO_2$ (8) - раствор после выщелачивания и фильтрации гидролизируют в батареи аппаратов с пневматическим **перемешиванием.** Гидролиз производится непрерывно, снижая постепенно температуру до около 40-45°C. Алюминат натрия разлагается в 52% за 72 часа.

Классификация и сгущение (9) – из крайнего аппарата для гидролиза $Al(OH)_3$ вместе с раствором подают в гидросепаратор, в котором производится разделение зерна $Al(OH)_3$, а также разделение матричного раствора от гидроокиси алюминия. Прививку после фильтрации (10) подают в раствор $NaAlO_2$, , а $Al(OH)_3$ предназначенный/ для производства Al_2O_3 фильтруют и промывают.

Фильтрация и промывка Al_2O_3 (II) – шлам Al_2O_3 во время фильтрации промывают горячей конденсационной водой.

Кальцинирование (12) – промытую гидроокись алюминия направляют на кальцинацию, а затем как готовый продукт Al_2O_3 – на склад. Фильтрат после промывки $Al(OH)_3$ и матричный раствор выпаривается.

Выпаривание (13) – раствор, через теплообменник, подают в выпарную станцию, где испаривается вода. Концентрированный раствор, в котором осаждаются кристаллы соды, сгущают в аппаратах Дора, с целью разделения соды от раствора (14).

Каустификация соды (15) – раствор задают известковым молоком, с целью превращения Na_2CO_3 в $NaOH$. Осажденный шлам ($CaCO_3$) фильтрируют, а щелочной раствор подают в шаровую мельницу бокситов, с целью растворения шлама после выщелачивания.

4.2 Технико-экономические показатели расхода на I т Al_2O_3 (мет. Баера)

каустическая сода	т	–	0,16
боксит	т	–	2,90
известь	т	–	0,07
пар 80-90 атм	т	–	3,15
пар 3,5 атм	т	–	2,24
мазут	т	–	0,075
электроэнергия	кВтЧ	–	295
вода (технолог.)	$м^3$	–	6
вода (для охлажд.)	$м^3$	–	4
коагулятор			0,004

По методу Баера образуются отходы так называемый "красный шлам", который в количестве около 1,9 тIт Al_2O_3 – направляют на отвал. Приложение Е /4.7/

Основной продукт – Al_2O_3	Технол. трад. Баера	Местонахожд. – Индонезия
Побочный продукт, отходы "красный шлам"	постоянный капитал	изменчивость цен –
Мощность завода 600 тыс.т в год	оборотный капитал – рабоч.дни в год –	период расчетный год

слагаемые затрат	единица расчета	единичная цена долл.	расход	стоимость производ. I т в долларах
едкий натрий	т	300	0,16	48,0
боксит	т	28	2,9	81,2
известняк	т	18,5	0,07	1,3
пар (70-80 атм)	т	4,5	3,15	14,2
пар	т	3,0	2,24	6,7
мазут	т	65,0	0,075	4,9
электроэнергия	кВтч	0,030	295	8,5
				165,2
стоимость раб. силы, администр. и другие материальные затраты		60% амортизации	x)	22,2
амортизации		5% инвестиционных затр.		37,5
				224,9

---

x) капитальные вложения на построение завода в Индонезии Битон Ислон мощностью 600 тыс.т/год (метод Баера) составили 450 млн. долларов т.е. 750 долларов на Iт Al_2O_3 в год.

5. Комплексное производство глинозема и портландского цемента спекально-распадовым методом Е. Гжимека (пат. №№ 43443, 43444, 44998)

одним из немногих методов получения глинозема из алюмосиликатов, технически и экономически разработанных в промышленном масштабе, является спекально-распадовый метод производства глинозема, разработанный Е. Гжимеком - профессором Горно-металлургической академии в Кракове, членом Польской Академии Наук.

Этот метод освоен на цементном заводе "Грошовице" около г. Ополе, где опытный цех производства глинозема работает с 1960 г., в котором получено около 70 тыс. т глинозема и гидроокиси алюминия и около 800 тыс. тонн цемента. На основе опыта завода "Грошовице" началось в Польше строительство завода по производству глинозема, мощностью ок. 100 тыс. т/год. Завод технологически связан с цементно-известковым комбинатом, производительностью 1,2 млн. т в год портландского цемента.

Профессором Гжимеком проводились исследования еще в довоенное время в Львовском политехническом институте, однако только после второй мировой войны технология, которая основана на явлениях полиморфизма ортосиликата кальция, усовершенствовалась и запатентировалась в стране и за рубежом. Явление полиморфизма ортосиликата кальция зависит от температуры. При охлаждении спека ниже

$675^{\circ}C$ образуется форма β $2CaO \cdot SiO_2$, которая в химически чистом ортосиликате кальция в температуре ниже $525^{\circ}C$, преобразовываясь в форму γ , самораспадается. Распад спека, содержащего ортосиликат кальция, вызван перемещением тетраэдров кремния и йонов кальция в пространственной решетке β-$2CaO \cdot SiO_2$, под влиянием снижающейся температуры. Правильное перемещение элементов, которое должно протекать быстро, из-за присутствия незначительных количеств попутных элементов, может притормозиться. Поэтому в данном методе соответствующее освоение процесса распада глиноземного спека, базирующегося на полиморфизме фазы -ортосиликата кальция, является главным условием, от которого зависит правильный ход технологического процесса и в главной мере экономика производства.

Уже в 1942 году на базе трудов проф. **Charles de Scille** пущено в действие два прототипных цеха производства глинозема из алюминосиликатного сырья (в виде золы, получаемой при спекании угля), один в Штрамберге в Чехословакии и второй в Рюдердорфе около Берлина. При проводимых на этих опытных заводах многолетних экспериментах, встречались весьма серьезные затруднения, заключающиеся в невозможности освоения в промышленном масштабе самораспада глиноземных, силикатных спеков и до конца войны работы на этих заводах не вышли за пределы экспериментов. После войны, по в/у причинам и другим непреодолимым трудностям в процессе непрерывной работы цементнообжигающей, вращающейся печи, неправильной экстракции и получении некачественного глинозема опытное производство прекратилось.

Большим успехом польских исследований было выявление причин стабилизирующего влияния йонов с высоким ионным потенциалом и высоким главным квантовым числом, на процесс полиморфического преобразования формы β на γ ортосиликата кальция, а также способов исключения стабилизирующего влияния этих ионов. Кроме того, полностью были освоены технические условия **востановительного** обжига и способа охлаждения глиноземного спека, обеспечивающие правильность процесса самораспада спека в промышленном масштабе. Степень самораспада глиноземного спека по спекально-распадовому методу Гжимека в среднем за год 97%.

Глиноземный спек, содержащий ортосиликат кальция, по методу Гжимека, распадается почти полностью во время его охлаждения в течение 30 мин., на пыль размером зерна 20 микронов. Такой эффект достигнут после проведения многолетних научно-исследовательских работ в Промышленном институте вяжущих строительных материалов в "Грошовицах" и Горно-металлургической академии в Кракове. В результате научных работ, а также многолетнего опытно-экспериментального производства, метод усовершенствовался. Улучшилась работа основного производственного оборудования и получены, наряду с высоким качеством глинозема и цемента, удовлетворительные экономические результаты.

Основным сырьем комплексного производства глинозема и цемента являются:

а) глиноземные глины с содержанием не менее 30% Al_2O_3,
весовым отношением $SiO_2 : Al_2O_3$ не больше, чем 2,
пропорцией $Al_2O_3 : Fe_2O_3$ не менее 5.

б) известняк с содержанием C_aCO_3 не менее 95%.

Могут применять также промышленные отходы, такие как карбидная известь или карбонат кальция, образующийся в производстве соды по методу сольвай и т.п.

Ниже приведены примеры состава глиноземного сырья, применяемого в ПНР

Наименование сырья	Основные компоненты в %				потеры обжига
	Al_2O_3	Fe_2O_3	SiO_2	CaO	
Илы из угольного разреза "Турув"	31,32	2,27	51,10	0,82	10,80
Сланцы из угольной шахты "Нова Руда"	31,15	2,85	34,16	1,47	30,00
Летучие золы из ТЭС "Турув"	32,96	6,86	50,87	2,38	3,00

5.а. Комплексное производство глинозема и портландского цемента из металлургического шлака по патентам №№ 196191, 198894, 203581

Спекально-распадовый метод Е. Гжимека известен за №№ польских патентов 43443, 43444, 44998. Он относился к комплексному производству глинозема и цемента. Новые направления в развитии этого метода с использованием полиморфизма ортосиликата кальция охватывают более широкий объем комплексного использования, наряду с глиноземом и цементом, также руд железа и образующихся в производстве глинозема из бокситов по методу Баера "красных шламов". Этот метод позволяет извлекать TiO_2, если данное сырье содержит двуокись титана, а также содержащиеся в рудах щелочи. Новый метод, запатентированный в Польше, под номером Р-198894, Р-203581, Р-196191, а также в США №4149898, является собственностью Горно-металлургической академии в Кракове.

Новый метод заключается в вызывании самораспада расплавленного металлургического шлака в температуре сверх 1500°С, распад которого из-за полного стеклования этого шлака, не был до сих пор освоен. В соответствии с этим методом глиноземное сырье или "красный шлам" смешивают с известняком, расплавляют и восстанавливают, с целью извлечения железа, а затем цемента и глинозема, а при переработке "красных шламов" можно еще получить двуокись титана и щелочи. Извлечение щелочей происходит при расплавлении шихты в температуре 1500°С в присутствии избытка окиси кальция, которые в данных условиях возгоняются и выделяются с выхлопными газами.

После выплавки железа, расплавленный шлак охлаждается в соответствии с кривой, указанной в патентном описании. Кривая охлаждения расплавленного шлака указывает температуры, в пределах которых образуются алюминаты кальция и ортосиликат кальция. Правильное охлаждение расплавленного шлака позволяет кристаллизировать алюминат кальция $I2CaO\cdot 7Al_2O_3$ в его высокотемпературной, полиформной форме, которая легко выщелачивается водным раствором Na_2CO_3, а также ортосиликат кальция из жидкой фазы и получать большие его кристаллы.

В температуре ниже $700^{\circ}C$ сплав может обрабатываться ультразвуками или резонансными вибрациями высокой частоты. В результате соответствующего охлаждения и внешних импульсов в стекловавшейся фазе алюмината образуются кристаллические зародыши ортосиликата кальция, которые стимулируют образование изоморфных кристаллов высокотемпературной полиформной формы $I2CaO\cdot 7Al_2O_3$.

Такого рода обработка ускоряет самораспадение сплава с одновременным достижением высокой степени автодезинтеграции охлаждаемого материала. Приведенный способ термообработки сплава с содержанием γCa_2SiO_4 и $I2CaO\cdot 7Al_2O_3$ позволяет его полному самораспаду на пыль с размером зерна около 30 микронов.

6. ОПИСАНИЕ ПРОЦЕССА ПРОИЗВОДСТВА ГЛИНОЗЕМА И ПОРТЛАНДСКОГО ЦЕМЕНТА СПЕКАЛЬНО-РАСПАДОВЫМ МЕТОДОМ Е. ГЖИМЕКА

6.1 Производство глинозема по спекально-распадовому методу охватывает следующие основные технологические операции (технологическая схема - рис.I)

Получение самораспадающегося спека.

Глиноземное сырье и известняк в соответствующих пропорциях размолачивают в шаровых мельницах (1), уединяют в коррекционных аппаратах (2), с целью доведения до кондиции химического состава, а затем обжигают во вращающейся, цементной обжигающей печи (3). Полученный спек подают на охлаждающую установку (4), где во время охлаждения, вследствие полиморфных преобразований ортосиликата кальция (внутриструктурные перемены, происходящие в кристаллах, находящихся в спеке минералов), самораспадаются, образуя, вместо твердого спека с гранулами около 50 мм диаметра, мелкую пыль размером с зерно около 0,02мм. Полученная без применения мельниц, самораспадающаяся пыль с большой специфической поверхностью около 10000 $см^2/г$ является исходным для производства глинозема.

Экстракция силикатов.

Пыль, полученная в результате распада спека, экстрагируется 6%-ым раствором карбоната натрия в противотоке (5), с целью растворения содержащихся в пыли алюминатов кальция и получения растворимого метаалюмината натрия:

а) $CaO\cdot Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CaCO_3$

б) $I2CaO\cdot Al_2O_3 + I2Na_2CO_3 + 5H_2O = I4NaAlO_2 + I2CaCO_3 + I0NaOH$

Фильтрация поэкстракционного раствора.

Водный раствор метаалюмината натрия отделяют от осадка (содержащего ортосиликат кальция и карбонат кальция) путем непрерывной декантации и фильтрации на тарелочном вакуум-фильтре (6).

Обескремнивание.

В процессе экстракции алюмината кальция, в раствор попадает незначительное количество кремнезема из ортосиликата кальция. Для обескремнивания (8) применяют известковое молоко (7). Процесс происходит при обычном давлении в температуре несколько ниже температуры кипения, в соответствии с реакцией:

а) $2Na_2SiO_3 + 2NaAlO_2 + Ca(OH)_2 + 2H_2O \longrightarrow$
$\longrightarrow CaO\cdot Al_2O_3\cdot 2SiO_2 + 6NaOH$

Побочная реакция, которая имеет место, заключается в том, что не полностью использованная в процессе экстракции сода, реагирует с известковым молоком и частично образуется едкий натрий в соответствии с реакцией:

б) $Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$

Раствор метаалюмината натрия декантируют, а затем фильтруют и подают в карбонизаторы (9).

Карбонизация.

Раствор после обескремнивания карбонизуют выхлопными газами из цементных или известкообжигающих печей после их очистки в скрубберах.
В этом процессе происходит реакция:

а) нейтрализация гидроокиси натрия
$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

б) гидролиз метаалюмината натрия и осаждение нерастворимых гидроокисей алюминия
$2NaAlO_2 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3$

в) в дальнейшем процессе карбонизации образуется кислый карбонат натрия
$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$

Регенерация.

Регенерация имеет целью обратно превратить кислый карбонат натрия в карбонат натрия. Регенерацию (13) производят известковым молоком. Раствор карбоната натрия после добавления соды (14) направляют обратно в экстракцию (5).

Кальцинирование.

Последние фазы производства глинозема - фильтрация (II) и кальцинирование (12) гидроокиси алюминия. Кальцинирование - это термическое обезвоживание и удаление кристаллизованной воды из гидроокиси алюминия. Кальцинирование производится во вращающейся печи или в печи с кипящим слоем (флюидизационной), отапливаемой мазутом или газом.

Производство цемента.

Шлам, полученный в процессе экстракции и фильтрации, направляют для производства клинкера мокрым методом или через сушилку для производства портландского клинкера сухим способом. После фильтрации шлам (6), содержащий прежде всего γ ортосиликат кальция, смешивают с размолотым известняком (15). Смесь обжигают в цементной вращающейся печи (17) и получают портландский клинкер, который вместе с гипсом размолачивают на цемент (18). По сравнению с классическим сырьем, технологическая ценность поэкстракционного остатка заключается в том, что он состоит из ортосиликата кальция с двумя связанными молекулами CaO, что в процессе обжига цементного клинкера влияет на ускорение связывания третьей молекулы CaO в кристаллическую решетку алита, главного компонента портландского цемента.

Этот метод, по сравнению с классическим методом обжига клинкера, характеризуется значительно меньшим расходом тепла, необходимого для диссоциации карбоната кальция, т.к. две третьих CaO, нужного для образования алита вводится в связанной форме в ортосиликате кальция и таким образом не требуется дополнительных расходов тепла на диссоциацию 3-х частей карбоната кальция на I часть SiO_2, содержащихся в классическом сырье. Полезным является также высокое раздробление ортосиликата кальция, с исключительно большой специфической поверхностью. Содержащийся в шламе ортосиликат кальция с островной структурой является значительно более активным, чем силикат в классическом сырье со слоистой или скелетной структурой. Упомянутые свойства поэкстракционных остатков, содержащих γ ортосиликат кальция, в случае их применения в качестве сырья для производства портландского клинкера, позволяют достичь роста производительности вращающихся **печей не менее, чем на 25% по сравнению** с методом производства клинкера из классического сырья.

6.2 Технико-экономические показатели на I т Al_2O_3 по методу Е. Гжимека (пат №№ 43443, 43444)

сода (Na_2CO_3)	- 0,18
летучие золы	- 3,8
известь (CaO)	- 0,15
угольная мелочь (30% золы; 4000 ккал/кг)	- 2,0
пар (3,0 атм)	- 3,0
гарное масло (9000 ккал/кг)	- 0,075
электроэнергия кВтч	- 1300
вода (технолог.) $м^3$	- 5
вода (для охлажд.) $м^3$	- 10
цемент портландский	- 10

6.3 По спекально-распадовому методу не образуются никакие отходы - даже выхлопные газы из вращающихся печей используются частично в процессе гидролиза алюмината натрия.

Допускаемый уровень шума в производственных помещениях в польской цементной промышленности составляет 90 дБ/А/. Измерение шума производится сонометром с фильтрами терциево-октавовыми. Шум записывается на специальном магнитофоне датского производства, а запись анализируется в лаборатории.

6.4 По мировым стандартам на заводе допускается концентрация пыли 0,1 - 0,15 г/ м^3. В Польше предельную концентрацию пыли для каждого района устанавливают Воеводские национальные советы. Для цементного завода "Новины", при котором строится цех, предельная концентрация пыли установлена на 100 кг/час из одной вращающейся печи. Определение пыльности производится при помощи кониметра РО-2 производства ЗАМ-Кенты. Периодическое зондирование воздуховедов.

Приложение Е

Основной продукт - глинозем; технол. - Е. Гжимек; местонахождение - цементный завод "Новины"
побочный продукт - портландцемент; постоянный капитал - оборотный капитал - изменчивость цен -
территория завода - 19 га
производство - 100 тыс.т/год Al_2O_3
1300 тыс.т/год цемента
количество раб. дней в год - 314
расчет по проекту

Себестоимость I тонны цемента ≅ 20 долл. США

слагаемые издержек	расчетная единица	цена за единицу	расход	стоимость производства в $
Переменные издержки				
сырье:				
сода (Na_2CO_3)	т	110,0	0,18	19,8
летучие золы	т	2,6	3,8	9,9
известь	т	18,5	0,15	2,8
угольная мелось (30% золы, 4000 ккал/кг)	т	12,0	2,0	24,0
пар (3атм)	т	3,0	3,0	9,0
гарное масло (9000ккал/кг)	т	65,0	0,075	4,9
электроэнергия	кВТч	0,030	1300	39,0
				109,4
рабочая сила, ремонты, администрация				
остальные издержки		60% от аммортизации		21,0
амортизация		6%		34,4
			Всего	164,8

Капитальные вложения на 1 т Al_2O_3 /год - 24.600 злотых.
Стоимость инвестиционного доллара 43,2зл. Таким образом, капитальные затраты на производство глинозема по методу Гжимека - 574 /IтAL_2O_3/ год.

При капитальных затратах на I т цемента /год 3800 зл. т.е. 88 долл.

6.а.1 Основные операции технологического процесса (технологическая схема - рис. 3)

Производство глинозема охватывает следующие основные операции:

- получение самораспадающегося шлака,
- экстракция алюминатов,
- фильтрация раствора после экстракции,
- приготовление известкового молока,
- обескремнивание,
- карбонизация
- регенерация,
- кальцинирование,
- производство цемента.

Подготовленная железная и глиноземная руды (I) вместе с негашеной размелченной известью (2) плавится в металлургической печи (3). Полученный чугун подвергается дальнейшей металлургической обработке, а образовавшийся шлак выщелачивают водным раствором карбоната натрия (5). Дальнейшая переработка алюмината натрия в окись алюминия производится по методу Е. Гжимека, патент №43443 и 43444. Остаток после выщелачивания (6) может непосредственно обжигаться на портландской клинкер (17) или корректироваться песком или известняком.

6.а.2 Технико-экономические показатели на I т Al_2O_3 по методу Е. Гжимека, патент №№ 196191, 198894, 203581

сода(Na_2CO_3)	-	0,08
металлургический шлак	-	5,96
негашеная известь	-	0,35
пар (3атм.)	-	2,5
гарное масло	-	0,075
электроэнергия кВтч	-	415
цемент портландский	-	5,0

При производстве I т Al_2O_3 получается также около 3,0 тонн чугуна.

6.а.3 По этому методу, как и по предыдущему, не образуются никакие производственные отходы – даже выхлопные газы из вращающихся цементных печей частично используются при гидролизе алюмината натрия.

Приложение Е (6а.7)

основной продукт – Al_2O_3
побочный продукт – цемент
территория завода – 9 га
производство – 68 тыс.т/год

технология – Е. Гжимек.
постоянный капитал –
оборотный капитал –
количество рабочих дней в год – 300

Место нахождения –
изменчивость цен –
период –
расчетный год –

слагаемые издержек	расчетная единица	цена за единицу долл.	расход	стоимость производства долл.
Переменные издержки				
сырье:				
сода (Na_2CO_3)	т	110	0,08	8,8
металлургический шлак	т	7	4,00	28,0
негашеная известь	т	18,5	0,35	6,5
пар (3атм)	т	3,0	2,5	7,5
гарное масло	т	65,0	0,075	4,9
электроэнергия	кВтч	0,03	415	12,5
				68,2
рабочая сила, ремонт администрация, остальные материальные издержки				21,0
амортизация				34,1
Всего себестоимость				123,3 долл.

Себестоимость производства цемента = 20 долларов

Инвестиционные издержки на 1 т цемента/год = 88 долларов

СОПОСТАВЛЕНИЕ ТЕХНИКО-ЭКОНОМИЧЕСКИХ ПОКАЗАТЕЛЕЙ ПРОИЗВОДСТВА ГЛИНОЗЕМА ПО МЕТОДУ Е. ГЖИМЕКА С МЕТОДОМ ПО БАЕРУ (7.1)

Метода Баера		Метод Гжимека пат.№43443, 43444		Метод Гжимека пат. №№ 196191, 198894,203581	
каустическая сода	- 0,16	сода (Na_2CO_3)	- 0,18	сода(Na_2CO_3)	- 0,08
боксит	- 2,90	летучие золы	- 3,8	металлург. шлак	- 4,90
известь	- 0,07	известь(CaO)	- 0,5	известь (CaO)	- 0,35
пар (80-70 атм.)	- 5,15	угольная мелочь (25% золы, 5000 ккал/кг)	- 2,0	пар (3 атм)	- 2,5
пар (3,5атм)	- 2,24	пар (3 атм)	- 3,0		
мазут	- 0,075	гарное масло (9000 ккал/кг)	- 0,075	гарное масло	- 0,075
электроэнергия кВтч	295	электроэнергия кВтч	1300	Электроэнергия кВтч	415
вода $м^3$ (технологическая)	- 6	вода $м^3$ (технологическая)	- 5	вода $м^3$ (технологическая)	- 6
вода $м^3$ (для охлаждения)	- 4	вода $м^3$ (для охлаждения)	- 10	вода $м^3$ (для охлаждения)	- 4
коагулент	- 0,004	портландский цемент	- 10	портландский цемент	- 5,0

Приложение F

отрасль сопоставления	традиционная технология (Баера)	безотходная технология Е. Гжимека		разница	разница
		по патентам №№ 43443 и 43444	по патентам №№ 196191, 198894 203851	2-3	2-4
I	2	3	4	5	6
материалы и энергия	132,7 долл./ на I т Al_2O_3	75,5 долл. на I т Al_2O_3	53 долл. на I т Al_2O_3	59,2 долл.	79 долл.
отходы	красный шлам	нет	нет	-	-
оборудование для защиты и контроля загрязнений	нет данных	электрофильтры 23 долл. на I т Al_2O_3 в год (в инвестиционных затратах)	электрофильтры 10 долл. на I т Al_2O_3 в год (в инвестиционных затратах)	- -	- -
единичное количество отходов	1,9 т красного шлама на I т Al_2O_3	нет	нет	-	-
инвестиционные издержки	750 долл. на I т Al_2O_3 в год	574 долл. на I т Al_2O_3 в год	574 долл. на I т Al_2O_3 в год	176 долл.	176 долл.
стоимость производства	194 долл. на I т Al_2O_3 в год	128 долл. на I т Al_2O_3 в год	109 долл. на I т Al_2O_3 в год		
другие сопоставимые данные					

7. Полученный по спекально-распадовому методу Е. Гжимека глинозем характеризуется исключительной чистотой и высоким качеством, пригодным для производства алюминия. Полученный этим методом глинозем содержит следующие загрязнения:

содержание	Na_2O	0,I5 - 0,30%
	SiO_2	0,02 - 0,04%
	Fe_2O_3	0,007- 0,0I%

Глинозем имеет дополнительные преимущества - он не содержит вредных следовых загрязнений окисью ванадия, хрома, марганца, меди, цинка и других. Насыпной вес Al_2O_3 - около 800 г/л.
Обладает свойствами фтора, выделяющегося в процессе электролиза. Этих свойств не имеет окись алюминия, полученная по методу Баера.

Продукт полностью пригоден для электролитического производства алюминия. Может также применяться в других отраслях промышленности.

8. Необходимость дальнейших исследований и совершенствования малоотходной и безотходной технологии.

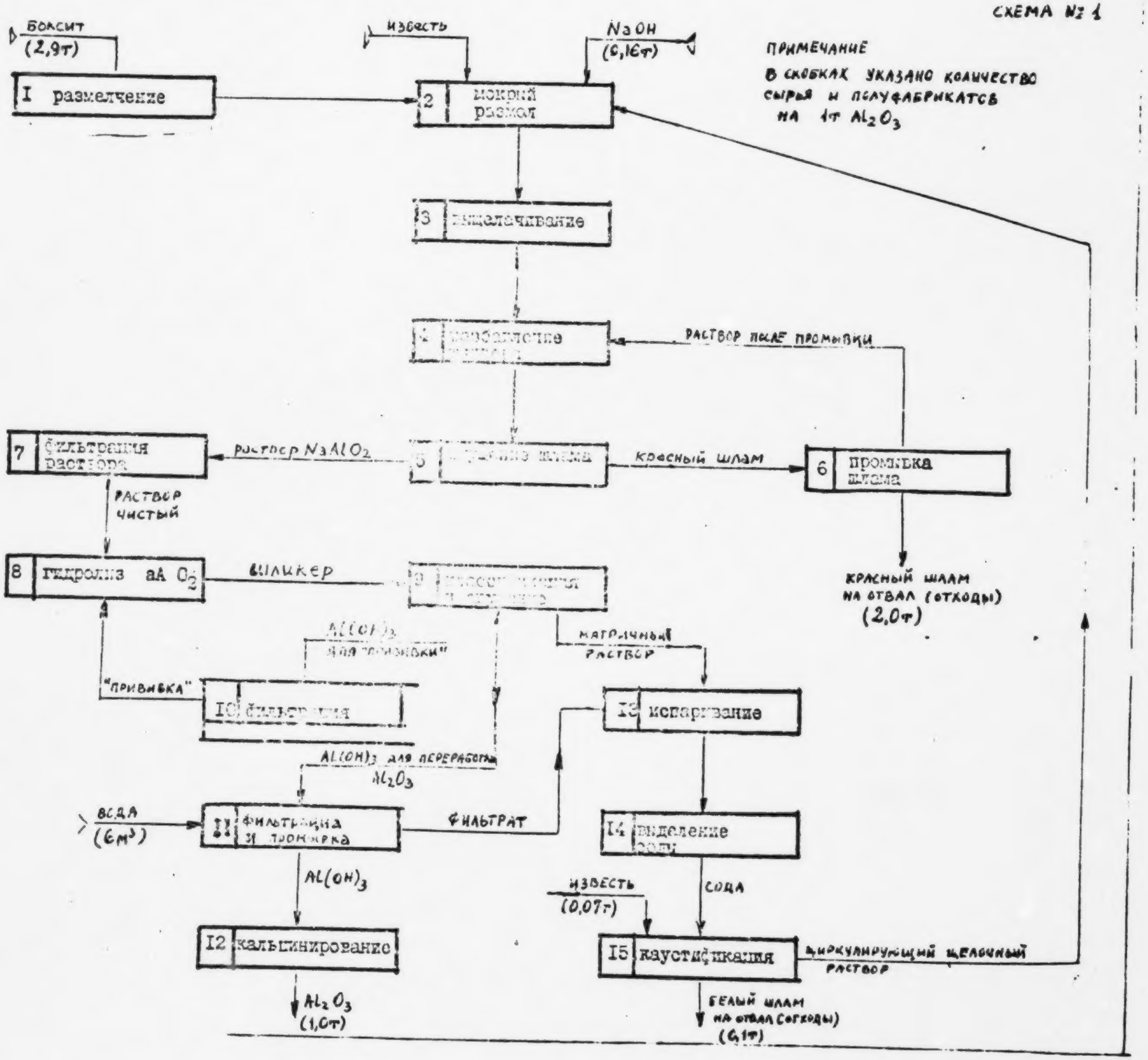
9. Организация, представляющая монографию, - Межведомственный институт строительных материалов и огнеупоров Горно-металлургической академии, г. Краков.

10. Дата составления - 1979 год.

ТЕХНОЛОГИЧЕСКАЯ СХЕМА ПРОИЗВОДСТВА ОКИСИ АЛЮМИНИЯ МЕТОДОМ БАЕРА

ПРИЛОЖЕНИЕ D

СХЕМА № 1


БОКСИТ (2,9т)
I размельчение
ИЗВЕСТЬ
NaOH (0,16т)
2 мокрый размол
3 выщелачивание
4
РАСТВОР ПОСЛЕ ПРОМЫВКИ
5
КРАСНЫЙ ШЛАМ
6 промывка шлама
КРАСНЫЙ ШЛАМ НА ОТВАЛ (ОТХОДЫ) (2,0т)
РАСТВОР $NaAlO_2$
7 фильтрация раствора
РАСТВОР ЧИСТЫЙ
8 гидролиз аА O_2
ШЛИКЕР
9
$Al(OH)_3$ для "прививки"
"ПРИВИВКА"
I0 фильтрация
МАТОЧНЫЙ РАСТВОР
I3 испарование
$Al(OH)_3$ для переработки Al_2O_3
ВОДА (6м³)
II фильтрация и промывка
ФИЛЬТРАТ
I4 выделение соды
$Al(OH)_3$
СОДА
ИЗВЕСТЬ (0,07т)
I2 кальцинирование
I5 каустификация
ЦИРКУЛИРУЮЩИЙ ЩЕЛОЧНЫЙ РАСТВОР
Al_2O_3 (1,0т)
БЕЛЫЙ ШЛАМ НА ОТВАЛ (ОТХОДЫ) (0,1т)

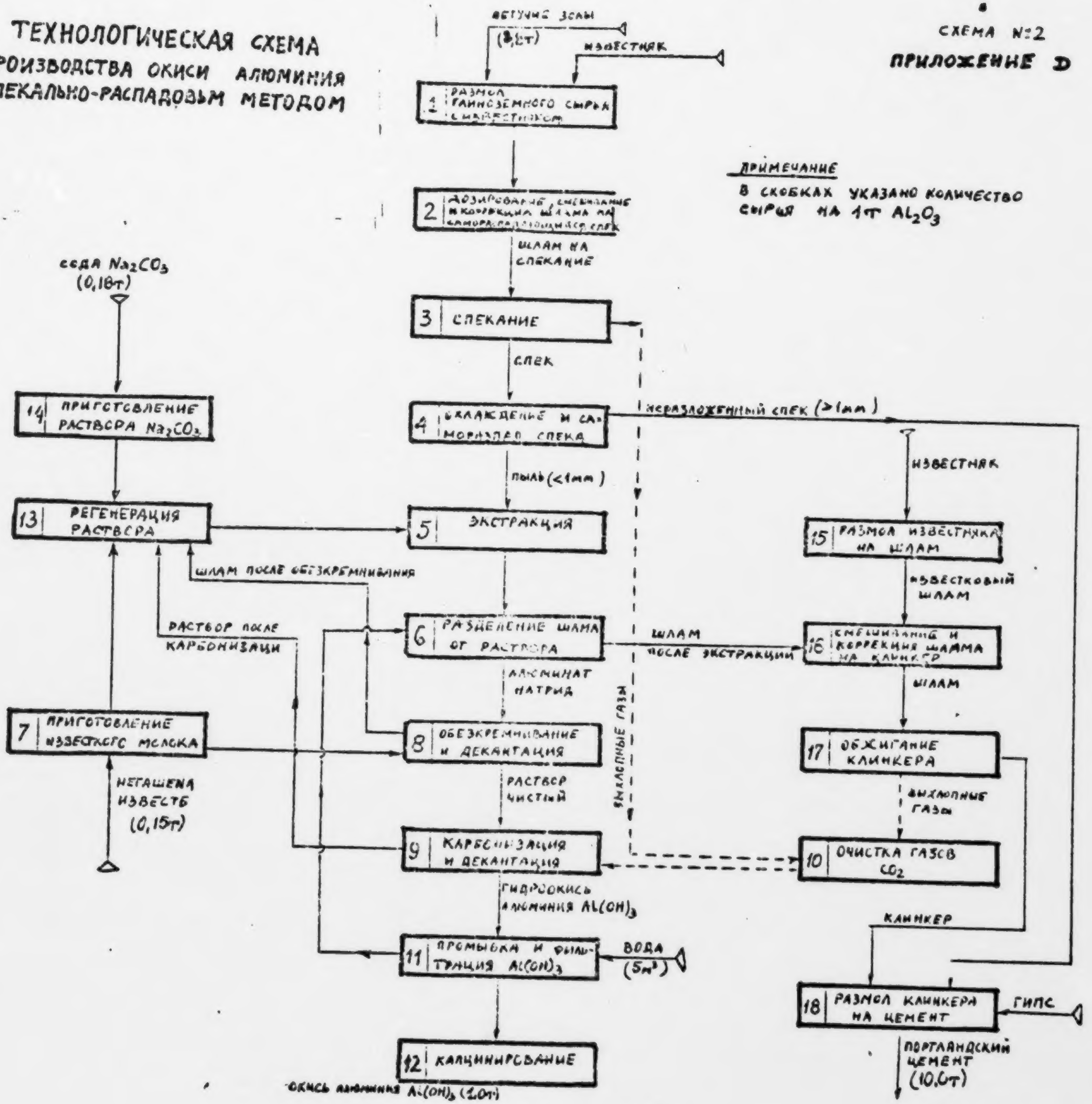
ПРИМЕЧАНИЕ

В СКОБКАХ УКАЗАНО КОЛИЧЕСТВО СЫРЬЯ И ПОЛУФАБРИКАТОВ НА 1т Al_2O_3

СХЕМА №2

ПРИЛОЖЕНИЕ D

ТЕХНОЛОГИЧЕСКАЯ СХЕМА ПРОИЗВОДСТВА ОКИСИ АЛЮМИНИЯ СПЕКАЛЬНО-РАСПАДОВЫМ МЕТОДОМ


ЛЕТУЧИЕ ЗОЛЫ (3,2т)
ИЗВЕСТНЯК
1 РАЗМОЛ ГЛИНОЗЕМНОГО СЫРЬЯ С ИЗВЕСТНЯКОМ
2 ДОЗИРОВАНИЕ, СМЕШИВАНИЕ И КОРРЕКЦИЯ ШЛАМА НА САМОРАСПАДАЮЩИЙСЯ СПЕК
ШЛАМ НА СПЕКАНИЕ
3 СПЕКАНИЕ
СПЕК
4 ОХЛАЖДЕНИЕ И САМОРАЗПАД СПЕКА
НЕРАЗЛОЖЕННЫЙ СПЕК (>1мм)
ПЫЛЬ (<1мм)
5 ЭКСТРАКЦИЯ
6 РАЗДЕЛЕНИЕ ШЛАМА ОТ РАСТВОРА
АЛЮМИНАТ НАТРИЯ
8 ОБЕЗКРЕМНИВАНИЕ И ДЕКАНТАЦИЯ
РАСТВОР ЧИСТЫЙ
9 КАРБОНИЗАЦИЯ И ДЕКАНТАЦИЯ
ГИДРООКИСЬ АЛЮМИНИЯ $AL(OH)_3$
11 ПРОМЫВКА И ФИЛЬТРАЦИЯ $AL(OH)_3$
ВОДА ($5м^3$)
12 КАЛЦИНИРОВАНИЕ
ОКИСЬ АЛЮМИНИЯ $AL(OH)_3$ (1,0т)
СОДА Na_2CO_3 (0,18т)
14 ПРИГОТОВЛЕНИЕ РАСТВОРА Na_2CO_3
13 РЕГЕНЕРАЦИЯ РАСТВОРА
ШЛАМ ПОСЛЕ ОБЕЗКРЕМНИВАНИЯ
РАСТВОР ПОСЛЕ КАРБОНИЗАЦИИ
7 ПРИГОТОВЛЕНИЕ ИЗВЕСТКОГО МОЛОКА
НЕГАШЕНА ИЗВЕСТЬ (0,15т)
ВЫХЛОПНЫЕ ГАЗЫ
ИЗВЕСТНЯК
15 РАЗМОЛ ИЗВЕСТНЯКА НА ШЛАМ
ИЗВЕСТКОВЫЙ ШЛАМ
ШЛАМ ПОСЛЕ ЭКСТРАКЦИИ
16 СМЕШИВАНИЕ И КОРРЕКЦИЯ ШЛАМА НА КЛИНКЕР
ШЛАМ
17 ОБЖИГАНИЕ КЛИНКЕРА
ВЫХЛОПНЫЕ ГАЗЫ
10 ОЧИСТКА ГАЗОВ CO_2
КЛИНКЕР
18 РАЗМОЛ КЛИНКЕРА НА ЦЕМЕНТ
ГИПС
ПОРТЛАНДСКИЙ ЦЕМЕНТ (10,0т)

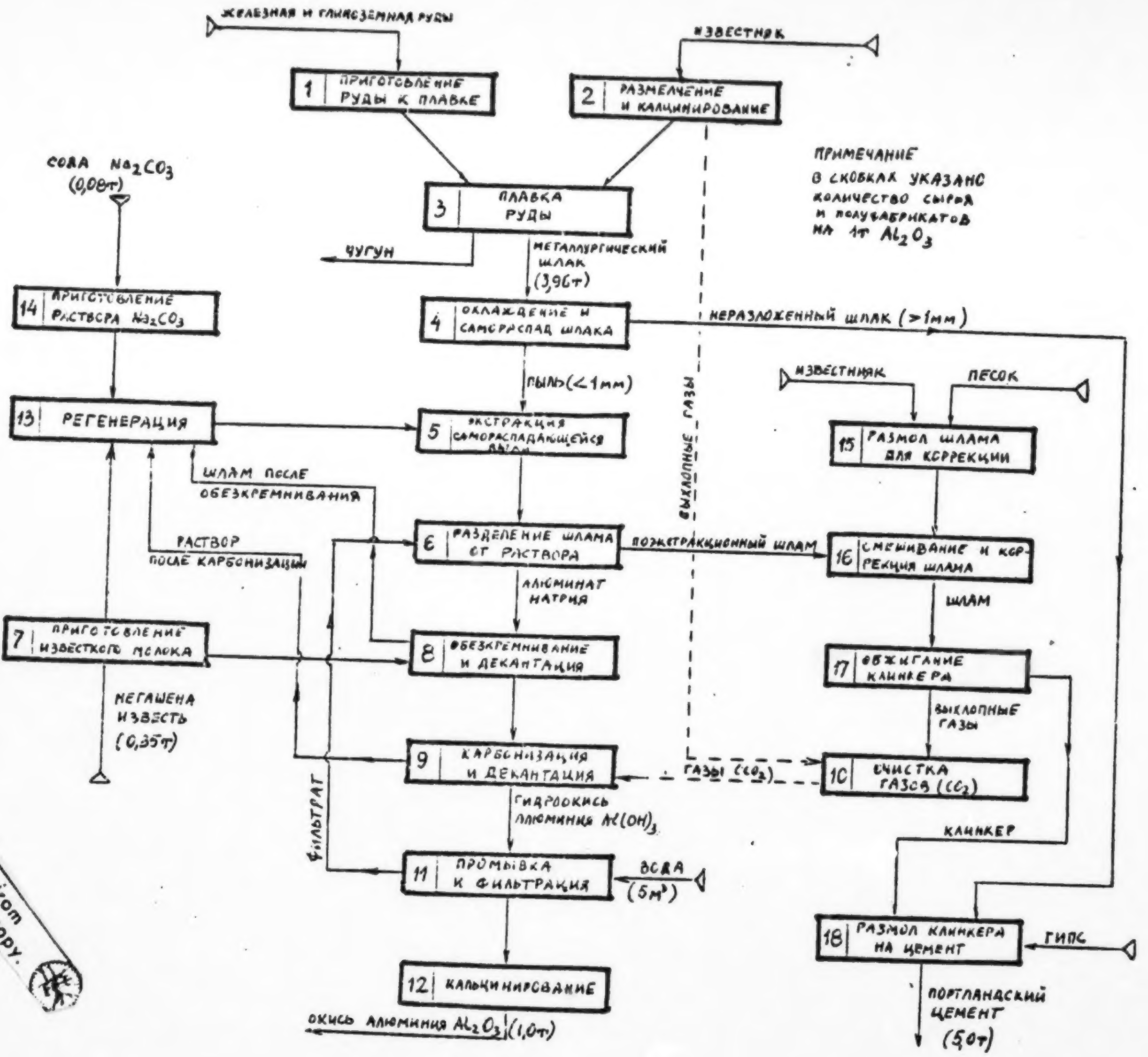
ПРИМЕЧАНИЕ

В СКОБКАХ УКАЗАНО КОЛИЧЕСТВО СЫРЬЯ НА 1т AL_2O_3

ТЕХНОЛОГИЧЕСКАЯ СХЕМА ПРОИЗВОДСТВА ОКИСИ АЛЮМИНИЯ ИЗ МЕТАЛЛУРГИЧЕСКОГО ШЛАКА

ПРИЛОЖЕНИЕ D

СХЕМА №3


ЖЕЛЕЗНАЯ И ГЛИНОЗЕМНАЯ РУДЫ
ИЗВЕСТНЯК
1 ПРИГОТОВЛЕНИЕ РУДЫ К ПЛАВКЕ
2 РАЗМЕЛЬЧЕНИЕ И КАЛЬЦИНИРОВАНИЕ
СОДА Na_2CO_3 (0,08т)
3 ПЛАВКА РУДЫ
ЧУГУН
МЕТАЛЛУРГИЧЕСКИЙ ШЛАК (3,96т)
14 ПРИГОТОВЛЕНИЕ РАСТВОРА Na_2CO_3
4 ОХЛАЖДЕНИЕ И САМОРАСПАД ШЛАКА
НЕРАЗЛОЖЕННЫЙ ШЛАК (>1мм)
ПЫЛЬ (<1мм)
ИЗВЕСТНЯК
ПЕСОК
13 РЕГЕНЕРАЦИЯ
5 ЭКСТРАКЦИЯ САМОРАСПАДАЮЩЕЙСЯ ПЫЛИ
ВЫХЛОПНЫЕ ГАЗЫ
15 РАЗМОЛ ШЛАМА ДЛЯ КОРРЕКЦИИ
ШЛАМ ПОСЛЕ ОБЕЗКРЕМНИВАНИЯ
РАСТВОР ПОСЛЕ КАРБОНИЗАЦИИ
6 РАЗДЕЛЕНИЕ ШЛАМА ОТ РАСТВОРА
ПОЭКСТРАКЦИОННЫЙ ШЛАМ
16 СМЕШИВАНИЕ И КОРРЕКЦИЯ ШЛАМА
АЛЮМИНАТ НАТРИЯ
ШЛАМ
7 ПРИГОТОВЛЕНИЕ ИЗВЕСТКОГО МОЛОКА
8 ОБЕЗКРЕМНИВАНИЕ И ДЕКАНТАЦИЯ
17 ОБЖИГАНИЕ КЛИНКЕРА
НЕГАШЕНА ИЗВЕСТЬ (0,35т)
ВЫХЛОПНЫЕ ГАЗЫ
9 КАРБОНИЗАЦИЯ И ДЕКАНТАЦИЯ
ГАЗЫ (CO_2)
10 ОЧИСТКА ГАЗОВ (CO_2)
ФИЛЬТРАТ
ГИДРООКИСЬ АЛЮМИНИЯ $Al(OH)_3$
КЛИНКЕР
11 ПРОМЫВКА И ФИЛЬТРАЦИЯ
ВОДА (5м³)
18 РАЗМОЛ КЛИНКЕРА НА ЦЕМЕНТ
ГИПС
12 КАЛЬЦИНИРОВАНИЕ
ПОРТЛАНДСКИЙ ЦЕМЕНТ (5,0т)
ОКИСЬ АЛЮМИНИЯ Al_2O_3 (1,0т)

ПРИМЕЧАНИЕ
В СКОБКАХ УКАЗАНО КОЛИЧЕСТВО СЫРЬЯ И ПОЛУФАБРИКАТОВ НА 1т Al_2O_3

Reproduced from best available copy.

UNITED NATIONS
ECONOMIC
AND
SOCIAL COUNCIL

E

RESTRICTED
ENV/WP.2/5/Add.17
8 July 1981
ENGLISH ONLY

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM OF LOW- AND NON-WASTE TECHNOLOGY

Monograph

RECOVERY OF MATERIALS FROM URBAN SOLID WASTES

Transmitted by the Government of Spain

1 Identification of the industry

Sanitary and similar services. ISIC 1/ code : 9200

2. Basic characteristics of the production process

This process enables the recovery and reintroduction of materials from urban solid wastes into the consumption cycle. This naturally involves energy consumption, which is sufficiently compensated for by the saving obtained compared to manufacturing the said materials from virgin raw materials.

3. Names of the conventional processing technologies

Processes for disposing of urban solid wastes by incineration, sanitary landfill composting.

2. Description of the processes of conventional technology

4.1 Incineration

Disposal of urban solid wastes by combustion in fixed or moving-grate furnaces by adding excess air, with the possibility of adding standard fuels to increase the calorific value.

4.1.1 Description of the unit operations used

Refuse incineration consists of the following unit operations :
- Dumping into a pit
- Homogenization of the refuse
- Feeding into the furnace

1/ International Standard Industrial Classification of All Economic Activities (ENV/WP.2/[illegible].Annex).

- Drying and precombustion
- Combustion
- Purification of the fumes produced
- Cooling of the fumes
- Possible recovery of the heat
- Removal of slag

There are several systems of incinerating refuse, each of which has a different operating characteristic, although, basically, they consist of the above-mentioned unit operations.

4.1.2 Specificationoof the waste produced

Apart from fumes, slag and ashes equivalent to from 20 to 30 per cent of the weight of the refuse incinerated are produced in the incineration processes.

4.1.3 Treatment costs

The total costs of treating 60,000 t/year including amortization, maintenance and labour amount to 1,500 pesatas per ton treated, although this sum may vary according to the particular method used.

4.2 Controlled dumping with or without previous shredding

This is a procedure for disposing of refuse by depositing it in a selected place, on which a technical and ecological study has been carried out.

4.2.1 Description of the operating process used

- Preparation of the dump and leach-proofing, if necessary
- Dumping of the refuse
- Depositing in fine layers and then compacting
- Covering

There are several methods for making a controlled dump, depending upon the characteristics of the site.

4.2.2 Specification of the waste produced

The system of eliminating refuse by controlled dumping is a procedure which does not produce further solid waste although it generates liquid waste which percolates to the bottom of the dump and which requires control, in order to prevent subsequent ground- and surface-water pollution. Gases produced from the decomposition of organic components are also given off at a controlled dump.

4.2.3 Treatment costs

The total costs of treating 60,000 tons per year including amortization, maintenance and labour, amount to 500 pesatas per ton treated, although this som may vary accod to the method used.

4.3 Composting

This is a method for transforming and isposing of urban refuse which consists of concentrating organic components and subjecting them to slow or fast biological decompositio for transformation into compost (physical regenerator of soils).

4.3.1 Description of the operating process used

- Dumping of the refuse
- Mechanical or manual sorting of the bulky components
- Crushing
- Classification and concentration of the organic fraction
- Slow or fast decomposition
- Purification of the compost obtained.

There are several systems of composting the organic fractions, each of which has an operating system which is different from the others, although, basically, they consist of those mentioned above.

4.3.2 Specification of the waste produced

Large amounts of waste are produced with this treatment system. In general, all those large, inert or non-fermentable organic components may amount to 50 per cent of the refuse treated.

4.3.3 Treatment costs

The treatment costs including amortization, maintenance and labour are calculated to be 800 pesatas per ton of waste treated, depending upon the system of composting and disposing of the refuse.

5. Name and state of development of the low- and non-waste processing technology

ENADIMSA process

Name : Integral recovery of the components contained in Urban Solid Wastes.

State of development : The process is currently being developed industrially on an integrated recovery line of 15 t/h.

There is a pilot plant in ENADIMSA's "Juan Gavala" research Centre in El Cerro de los Angeles, Madrid (Spain), with a capacity of 10 t/h.

A plant with a capacity of 15 t/h has also been operating since 1977 in the town of Tournan in Brie (France), situated 35 km east of Paris.

Another plant with a capacity of 15 t/h was planned to be opened in Tarragona (Spain), in November 1979.

A plant for recovering combustible material, with a capacity of 20 t/h, was expected to be commissioned in Uppsala (Sweden) in May 1980.

6. Description of the low- and non-waste processing technology

The process consists of recovery and selective concentration of components contained in urban solid wastes by means of crushing, pneumatic sorting, decanting, semi-wet separation of paper and elastic, mechanical, magnetic and densimetrical sortings.

6.1 Description of the operating process used

The process starts with the dumping of the material (raw refuse) in a hopper/platform where it is fed by means of belt conveyors into a chain mill. The chain mill consists of a housing fitted with two shafts with chains rotating in opposite directions. The purpose of this primary mill is to split and open the plastic bags in which the refuse is usually contained, and to reduce the larger materials, breaking the fragile components such as glass, slag and ceramic materials into smaller pieces.

When the refuse leaves this mill, there is a pneumatic collector which separates a light fraction that is carried by pneumatic transport to a decanting cyclone. This fraction consists mainly of paper, cardboard, plastic and fabrics.

The material not sorted by the pneumatic collector undergoes mechanical sorting in a 65mm mesh, rotary screen.

Material over 65 mm is sorted magnetically by means of a conventional over-band separator. The resulting fraction consists of iron and tin cans.

The material which is rejected in this magnetic separation is considered incinerable material. It consists of plastic, paper, cardboard and fabrics not sorted in the pneumatic collector, along with other combustible materials.

Material under 65mm undergoes magnetic sorting by means of a magnetic drum separator. The magnetic fraction recovered consists mainly of bottle tops.

The rest of the material, containing organic matter and glass, follows the process and is sieved again through a 15mm rotary screen.

The product between 15 and 65mm is the organic component.

The product under 15mm is sorted gravimetrically in a hydraulic screen in which two components are concentrated :

- inorganic matter under 15mm consisting of glass, ceramics and slag;
- organic matter under 15mm

The light fraction undergoes semi-wet sorting in order to recover plastics and obtain a fraction consisting mainly of cellulose-like products. The plastics are later cleaned by washing.

The inorganic fraction is cleaned by flotation, giving high quality glass concentrate.

Of the magnetic material over 65mm, the magnetic tin fraction is concentrated.

It is noteworthy that starting with material originally of no obvious value, products may be obtained which, either directly or with subsequent transformations, have useful possibilities.

This series of operations enables the following components to be concentrated :

Component	per cent
Paper	9 - 13
Plastic film	2 - 3
Plastic bottles	1 - 1.5
Organic matter for composting	40 - 60
Glass	2 - 3
Magnetic tin scrap material	1.5- 2.5

(Data based on average composition of Urban Solid Wastes from Madrid)

These concentrated components may be reintroduced into the consumption cycle with a resultant saving in energy and raw materials.

6.2 Specification of materials and energy required.

The energy consumption for a capacity of 60,000 t/year is 36 kWh per ton treated.

6.3 Specifications of the form and amount of airborne, waterborne and solid wastes generated in the production process, and the control of waste produced

(a) Solids :

The capacity of one line is 15 t/h of solid refuse. Of this capacity, 20 to 25 per cent is considered solid waste to be disposed of by means of incineration or controlled dumping. However, these may be used as a potential source of energy for the same plant, as its calorific value ranges between 1,500 and 2,500 Kcal/kg. The systems for controlling pollution in the disposal of these rejected products are those commonly used in the conventional processes of incineration and controlled dumping.

(b) Water:

This process requires 20 m^3/h of water for different stages (hydraulic sorting, plastic washing, etc.). Some 80 per cent of this amount is recirculated in a closed circuit. The remaining 20 per cent is accounted for by the water contained in the treated organic components under 15mm, in the paper, and by evaporation losses. It is not necessary in any of these cases to carry out pollution control, since the organic matter passes on to a composting process and water pollution controls in the paper mills overcome possible pollution from processing recycled paper.

(c) Air:

The process uses air flows ranging between 5 and 8 m^3/s at atmospheric temperature. 100 per cent of the flow/used is released into the atmosphere after it has undergone dust purification treatment by means of a highly efficient bag or cyclone filter.

6.4 Treatment cost enabling its comparison with conventional technologies

For yearly capacities of 60,000 t/year, which is equivalent to one line of 15 t/h with two daily shifts, the total costs including amortization, maintenance and labour amount to 1,125 pesatas per ton treated. Of this total cost, account has not been taken of the positive item of income from the sale of by-products, as this is linked to market conditions (see table 1).

The latest data obtained in market studies carried out for this purpose give the following prices for materials recovered in Spain :

Component	Pesatas per ton
Paper	1 700
Plastic film	10 000 - 15 000
Plastic bottles	10 000 - 15 000
Organic matter	300 - 800
Magnetic tin products	7 000
Glass	1 500

7. Diagramatic comparison between the conventional technologies and the non-polluting or wasteless technology

See attached Diagram 7.

8. Identification of needs for further research and development with regard to the low- and non-waste technology

The main commitment would be to promote the market for the raw materials recovered in the process as in many cases virgin materials may be replaced by recovered materials.

9. Reporting organization

Empresa Nacional ADARO de Investigaciones Mineras, S.A.
(ENADIMSA)
Serrano 116, Madrid 6
Spain.

10. Date of report

September 1979

7. DIAGRAMATIC COMPARISON BETWEEN THE CONVENTIONAL TECHNOLOGIES AND THE NON-POLLUTING OR WASTELESS TECHNOLOGY

Areas of comparison	Conventional technology	Non-polluting or wasteless technology	Difference
Materials	a) Incineration b) Controlled dumping c) Composting	ENADIMSA recycling	Integral recovery of raw materials contained
Generation of refuse	a) Solids and gases b) Liquids c) Solids, liquids & gases	Solids	No polluting gases or liquids given off
Measures for controlling the pollution	The conventional ones in this kind of industry	The usual ones in the conventional technology	None
Waste produced	a) Slag and fumed b) Leached c) Organic, inert, leached and gaseous	Slag or inert solids depending on whether the matter rejected is incinerated or dumped	Less solid waste; with no gas and liquid waste
Investment	a) 2,5 MP/ton of NC b) 0,2 MP/ton of NC c) 1,0 MP/ton of NC	1,5 MP/ton NC	Average operation costs of the conventional techniques
Production costs	a) 1,500 pts/t b) 500 pts/t c) 800 pts/t	1,125 pts/t	Average operation costs between the conventional system
Other areas of comparison	b) Need for large surface, away from urban centres	Average use of land surface	Less surface used than in controlled dumping

a) Incineration
b) Controlled dumping
c) Composting
NC = Nominal capacity (t/day)
MP = Million pesatas

TABLE 1 - PRODUCTION COSTS

Costs	Units	Factor/unit cost	Units required/ ton treated	Cost/ton
VARIABLE COSTS				
- Raw materials	t	-	-	-
- Energy	Kw	3 pts/Kw	≃ 36 Kwh/t	108 pts/t
- Water	m^3	10 pts/m^3	0,5 m^3/t	5 pts/t
- Labour:				
Operation	Hours-man	800 pts/h-man	0,48 h-man/t	384 pts/t
Maintenance	Hours-man % labour	10% operation	-	38 pts/t
- Sundries	% cost energy	50%	-	54 pts/t
SUB-TOTAL VARIABLE COSTS				589 pts/t
FIXED COSTS				
- Overheads	% labour	60%	-	253 pts/t
- Local and industrial rates		-	-	-
- Depreciation	% fixed capital	10%	-	283 pts/t
SUB-TOTAL FIXED COSTS				536 pts/t
SUB-TOTAL PRODUCTION COSTS				1.125 pts/t
- Return rate	-	-	-	-
- Pollution control	-	-	-	-
TOTAL	-	-	-	1.125 pts/t

- Product: Urban Solid Wastes
- Capacity of the plant: 15 t/h
- Yearly capacity: 60,000 t/year
- Process: ENADIMSA
- Fixed capital: 170 MP
- Days worked/year: 300
- Location: Several
- Depreciation period: 10 years
- Envisaged years of operation: 10 years

UNITED NATIONS

ECONOMIC
AND
SOCIAL COUNCIL

E

RESTRICTED

ENV/WP.2/5/Add.18
10 July 1981

ENGLISH ONLY

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

LIQUID PHASE EXTRACTION OF MERCURY CONTAINED IN EFFLUENTS OF CHLORINE-CAUSTIC SODA MANUFACTURE

Transmitted by the Government of Spain

1. Identification of industry

Chlorine-caustic-soda manufacturing. ISIC[1] code : 3511

2. Basic characteristics of production process

Chlorine and caustic soda (or potash) are produced through brine electrolysis. This process is carried out in different types of electrolytic cells. The aspect of this industry of particular interest here is that based upon cell electrolysis with a mercury cathode, the predominant method in Europe, which consumes less energy and results in greater product purity than the other competing techniques.

As a consequence of the use of mercury, the process and waste streams from this industry may result in effluents with a high concentration of this element.

The information provided in this monograph refers to two technologies that have been designed especially to solve the contamination problem in two of these streams. Therefore, rather than a broad analysis of the universal technology used in the chlorine-soda industry, whose main facets are not, in any case, substantially modified by these technologies, two particular technologies will be described in this monograph. They are :

(a) the brine purification process to be used in electrolytic chlorine-producing cells;
(b) purification process for liquid effluents contaminated by mercury.

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex).

GE.81-42205

3. Name of conventional processing technology

Brine purification procedure through alkaline precipitation.

In a conventional old plant, the aqueous effluents were not treated. There are presently several processes that can be used to treat them, one of which is described in this monograph.

4. Description of the conventional processing technology

The following will deal only with the conventional technology of brine purification.

4.1 Description of the process

In manufacturing caustic soda and chlorine through sodium chloride brine, it is necessary to reduce the impurities introduced by the salt to a minimum, especially the cations of Ca, Mg and Fe. The classic procedure eliminates these cations through precipitation, by alkalinizing the brine with sodium hydroxide and adding sodium carbonate. Following this treatment, the brine is transferred to a settler in which the sludges formed by magnesium and iron hydroxides and calcium carbonate are separated from the brine, leaving a clear brine which is then transferr to storage tanks. After a pH adjustment, the brine is transferred to the electrolytic cells.

The sludges separated from the bottom part of the settler are made up of carbonates and hydroxides, which constitute 8 per cent of their weight, while the remainder is a concentrated sodium chloride solution. The sludges also contain about 20 ppm of mercury (Hg), on average, determined on a wet basis.

These sludges are normally sent to a sludge treatment unit (see 4.5), where the brine and mercury can be recuperated.

The residue left behind by this treatment can be eliminated in various ways, since it contains minor amounts of mercury.

4.2 Material specifications and energy requirements per m^3 of product

The average chemical product requirements for the treatment, obviously dependent on the quality of the salt employed, are :

Sodium carbonate	0.32 kg/m^3
Sodium hydroxide	0.32 kg/m^3

The energy requirements are 0.03 GJ/m^3 of treated brine. This amount includes the energy consumed in moving and heating the brine.

4.3 Specification of the forms and quantity of solid, waterborne and airborne wastes generated in the process

Some 3.5 kg of sludge per m^3 of treated brine are produced. These sludges contain about 20 ppm of Hg.

4.4 Specification of applicable standards on the emission of wastes

There are no concrete standards that regulate the discharge of sludges. Nevertheless, the existing standards on the discharge of liquid effluents should be applied. These standards vary according to factory location. They are the following :

- Coastal zones :	2g Hg/TCl_2 (daily average)
	1g Hg/TCl_2 (monthly average)
- Inland zones :	0.28g Hg/TCl_2 (daily average)
	0.14g Hg/TCl_2 (monthly average)

4.5 Specification of additional pollution control measures necessary for compliance with existing standards

The sludges that are separated in the settler (8 per cent of their weight is solid, while the remainder is brine) also contain about 20 ppm of mercury.

These sludges are subjected to a filtering treatment, which separates the brine they contain. The solid residue, in which the moisture content is very low - in the 5 to 15 per cent range, is treated in a stirred tank with hydro-chloric acid and sodium hypochlorite, in order to dissolve the mercury content (about 200 ppm based on the weight of the dried cake).

Following this treatment, the sludge is filtered, leaving behind a cake with low mercury concentration which can be taken outside the factory, and a water stream contaminated with mercury, which must be treated in an effluent demercurization plant, e.g., the MERCUREX process (see Point 5.B.) before it can be discharged.

4.6 Specification of the waterborne, solid and airborne waste discharges into the environment

Following the sludge treatment described in the previous section, a solid residue is left behind (0.35 kg/m^3 of the treated brine) containing about 10 ppm of mercury. The water obtained from the treatment of sludges, after being treated in a MERCUREX demercurization plant, contains 0.01 ppm of Hg and may be discharged.

4.7 Costs which allow a comparison of the L/NWT with conventional technology

These are summarized in Table 1.

5.A. Name and state of development of low- and non-waste processing technology :

Commercial name : SAMEX

Location : A functioning experimental plant, for commercial demonstrations and industrial tests in the EIASA factory at Palos de Moguer, Huelva (Spain). The plant began operating in June 1978 and has a treatment capacity of 12m^3/h of brine.

6.A Description of low- and non-waste technology

6.1.A Description of the process

The purification of brine in the SAMEX process is carried out through a selective extraction of the impurities, with a liquid-liquid system, which contacts the brine with an organic phase in which the extracting agent is dissolved.

The brine coming from the saturators is filtered to eliminate solid impurities and then moves on to the extraction phase, in countercurrent contact with the organic agent, gas-oil, which contains the extracting agent, an organic phosphoric acid, and a modifier which facilitates the separation phases after the extraction.

Where RH represents the extracting agent, the extraction of the Ca, Mg and Fe impurities may be expressed schematically in the following manner :

$$3RH + Fe^{+++} \rightleftharpoons R_3Fe = 3H^+$$

$$2RH + Mg^{++} \rightleftharpoons R_2Mg + 2H^+$$

$$2RH + Ca^{++} \rightleftharpoons R_2Ca + 2H^+$$

The aqueous effluent from the extraction phase is made up of brine, free of cation impurities, which are sent to the electrolytic cells after having passed through an activated carbon filter to eliminate any drag from the organic phase in the extraction, after the aqueous-organic contact.

The organic phase, containing the cations Ca, Mg and Fe is followed by a re-extraction or stripping stage in which it is purified by an acid treatment. It thus becomes suitable for being recycled once again in the extraction stage. The reaction that takes place during this stage is the displacement towards the left of the reactions previously described.

The aqueous effluent of this re-extraction phase is an aqueous acid solution with concentrations of Ca, Mg and Fe, which contains no mercury and which may therefore be drained away directly. The SAMEX process may be represented schematically by the block diagram in Figure 1.

6.2.A Material specifications and energy requirements per m^3 of product

The only energy consumption involved in the process is that needed for lighting purposes and moving the liquid by means of pumps and shakers. This consumption is estimated to be about 3.4 kWh/m^3.

The reagents necessary for the process are : sodium hydroxide to adjust the pH of the extraction, plus water and hydrochloric acid for the re-extraction stage. However, it is necessary to separate the organic phase lost through drag with the brine.

PRODUCT	kg/m^3 of brine
NaOH	0.7
HCl	0.7
H_2O	2.9
Organic products	0.002

6.3.A. Specification of the form and quantity of airborne, waterborne and solid wastes generated in the process

The composition of the plant effluent which is discharged is indicated in the column corresponding to stream No. 8 in the table of Figure 1.

It is not polluting, since it is an aqueous acid solution of calcium, magnesium and iron, and does not contain mercury. If necessary, it should be neutralized to pH 7.

6.4.A. Specification of applicable standards on the emission of wastes

Answered in section 4.4.

6.5.A. Specification of additional pollution control measures necessary for compliance with existing standards

With this process, no additional equipment is needed, since it does not produce sludges contaminated with mercury.

6.6.A. Specification of the waterborne, solid and airborne wastes released to the environment

Answered in 6.3.

6.7.A. Costs which allow a comparison of the low- and non-waste technology with conventional technology

These costs are given in Table 2.

7.A. Schematic comparison between the conventional and the low- and non-waste technology

7.1.A to 7.5.A : these points are summarized in Table 3.

7.6.A Other significant differences between the low- and non-waste technology and the conventional technology

One achieves a greater degree of purity with the SAMEX process than with conventional processes.

The installation requires much less space.

Finally, and quite apart from the mercury pollution problems, the SAMEX process avoids handling of the sludges, which would be produced in the process of purification through precipitation.

5.B. Name and state of development of low- and non-waste processing technology

Commercial name : MERCUREX

Location : Two operational plants, one in the Energia e Industrias Aragonesas, S.A., factory in Vilaseca, Tarragona (Spain), which began operating in July 1977 and another in the Energia e Industrias Aragonesas, S.A. factory in Sabiñanigo, Huesca (Spain), which began operating in November 1977. Both plants have been designed to treat 6 m^3/h of polluted water.

6.B Description of low- and non-waste technology

6.1.B. Description of the process

The elimination of mercury from the polluted water is carried out through a process of liquid-liquid extraction.

The liquid streams that come into contact are : an aqueous stream, made up of residual water, and an organic stream which extracts mercury from the aqueous phase.

The extraction process is preceded by a conditioning stage of the residual aqueous stream.

The residual water, generally alkaline, contains mercury in colloidal form and in the form of soluble mercury salts. The extraction only takes place when the mercury is in ionic form, thus making it necessary to oxidize the colloidal mercury before the residual water can be moved to the extraction phase, so that all the mercury it contains is in cationic form.

Oxidation is carried out in a stirred reactor using sodium hypochlorite as an oxidizing agent. Hydrochloric acid is added simultaneously to lower the pH of the residual water to the acid state, where oxidation is effected more easily.

After this oxidation stage, the aqueous stream is passed through a sand filter to retain the solid particles which the residual water carries along, and which, if not eliminated, could hinder the separation of the organic and aqueous phases in the extraction.

An excess of the oxidizer used in the dissolution of the colloidal mercury may destroy the extracting agent dissolved in the organic phase. To eliminate this problem, a reducer (sodium sulphite) is added to the aqueous stream before the extraction stage.

In the extraction process, two opposing streams come into contact : the water containing mercury and the organic phase. The latter extracts the mercury and is not soluble in water. This organic phase is made up of a dilutant, kerosene, in which the extracting agent (mercaptan) is dissolved, and a modifier whose task it is to favour the solubility of the organic compound which is formed and to facilitate the phase separation after extraction.

Where the RSH represents the extracting agent, the mercury extraction may be expressed by the following reactions :

$$RSH + Cl_2Hg \rightleftharpoons RSHgCl + HCl$$
$$2RSH + Cl_2Hg \rightleftharpoons (RS)_2Hg + 2HCl$$

Following extraction, a purified acidic aqueous effluent is obtained which is drained away, and an organic phase containing the extracted mercury. This organic phase is then taken to a re-extraction stage in which the mercury mercaptide is destroyed by adding an acid solution containing the anion Cl−, which can attract the mercury ion and favour re-extraction. This stage may be represented in the following reaction :

$$(RS)_2Hg + 2H^+ + 4\ Cl^- \rightleftharpoons 2RSH + HgCl_4$$

From this re-extraction stage one obtains a regenerated organic phase which is recycled to extraction and an aqueous phase containing the mercury, sodium chloride and hydrochloric acid, which is incorporated into the brine cycle of the chlorine-soda.

The MERCUREX process may be expressed schematically by the block diagram given in Figure 2.

6.2.B. Product specification and energy requirements per m^3 of product

- Energy requirements : The whole process is carried out at ambient temperature and, therefore, the only energy needed is that used for lighting and that used to power pumps and vibrators. This consumption may be estimated at about 1.5 kWh/m^3.

- Product requirements : The reagents needed are sodium hypochlorite, sodium sulphite, hydrochloric acid and sodium chloride, whose role in the process was defined in section 6.1.B.

On the other hand, it is also necessary to replace the organic phase lost through drag in the purified water, as well as the degraded extracting agent. Consumption is :

PRODUCT	kg/m^3 H_2O
NaOCl	0.05
Na_2SO_3	0.27
HCl	6.4
NaCl	3.5
H_2O	5.5
Extracting Agent	0.01

6.3.B Specification of the airborne, waterborne and solid wastes generated in the process

The composition of the currents leaving the plant (numbers 7 and 12) are given in the table in Figure 2. Of the two, only No. 7 leaves the factory, since No.12 is recycled to the electrolysis circuit.

6.4.B. Specification of the applicable standards on the discharge of wastes

See section 4.4.

6.5.B Specification of additional pollution control measures necessary for compliance with existing standards

No additional equipment is needed. The whole process is added to a plant manufacturing chlorine-soda using the mercury cathode method , and complies with the existing legislation on the emission of Hg in liquid effluents.

6.6.B. Specification of the waterborne, solid and airborne wastes discharged into the the environment

Answered in section 6.3.B. above.

6.7.B. Costs which allow a comparison of the low- and non-waste technology with the conventional technology

The comparison of the costs of the low- and non-waste technology is given in Table 4.

7.B. Schematic comparison between the low- and non-waste technology and the conventional technology

The MERCUREX process is an auxiliary industrial process which in itself does not produce any pollution. It is a process meant to eliminate mercury pollution in aqueous effluents resulting from the manufacture of chlorine through brine electrolysis with a mercury cathode. Therefore, it should not be compared with any other similar process. An adequate comparison should evaluate the pollution from the manufacturing process with or without the MERCUREX process incorporated.

7.1.B. Materials and energy requirements
and
7.4.B. Discharges of airborne, waterborne and solid wastes

These points have been considered under 6.B. above.

7.5.B. Investment requirements and production unit costs

The following table indicates the investment cost of consumption per unit in pesetas in 1979, for a plant which treats 10^3m/h of water containing 20 ppm of mercury.

Investment	35 M pesetas
Electric energy	2.1 pesetas/m^3
Reagents [a]	26.6 pesetas/m^3
Extractor	3.0 pesetas/m^3

a/ See point 6.7.B. for the credits to be discounted from this consumption

7.6.B. Other significant differences between low- and non-waste and conventional technolog technology

As previously stated in 7.B., the MERCUREX process cannot be compared with conventional processes.

8. Identification of need for further research and development with regard to the law and non-waste technology

Not treated.

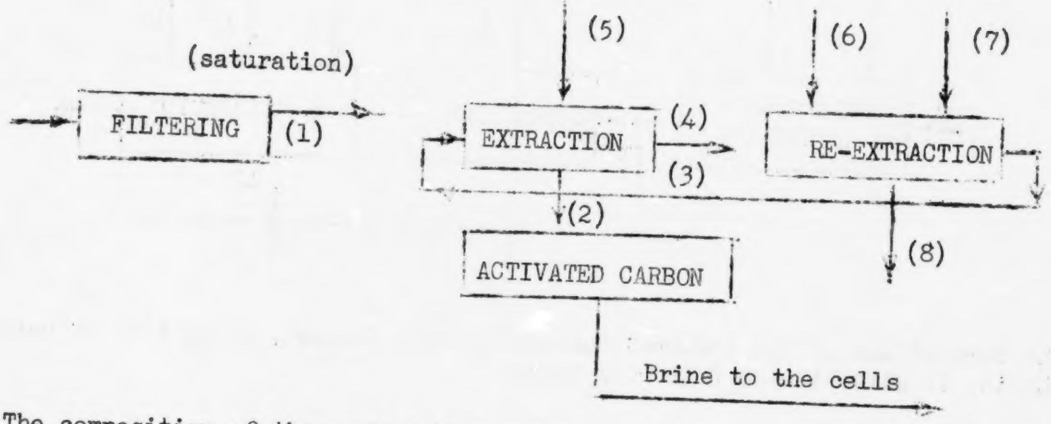
9. Reporting organization

The Ministry of Energy and Industry,
Directorate General of Technology and Industrial Safety,
Madrid,
Spain

10. Date of report

November, 1979

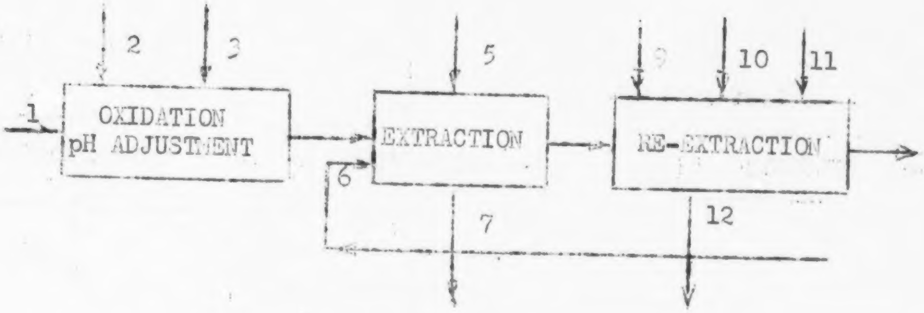
FIGURE 1


(saturation)
FILTERING
(1)
(5)
EXTRACTION
(4)
(3)
(2)
(6)
(7)
RE-EXTRACTION
(8)
ACTIVATED CARBON
Brine to the cells

The composition of the numbered currents in the diagram, for a 1 m^3/h treatment of brine, is summarized in the following table :

	1	2	3	4	5	6	7	8
H_2O, kg/h	864	867			2.7	2.9	1.7	4.6
NaCl,kg/h	306	307						0.3
NaOH,kg/h					0.7			
HCl,kg/h							0.7	0.2
Ca,ppm	150	<1		294				30,000
Mg,ppm	30	1		54				5,510
Fe,ppm	2	0.1		1.8				306
Hg,ppm	10	10						
Organic, kg/h			395	395				

FIGURE 2


1
2
3
OXIDATION
pH ADJUSTMENT
5
EXTRACTION
6
7
9
10
11
RE-EXTRACTION
12

The composition of the numbered currents in the diagram, using 1 m^3 of water/h as the basis, is given in the following table :

	1	2	3	4	5	6	7	8	9	10	11	12
Hg,ppm	25			25		1	0.01	13.5				1000
Cl_2,ppm				50								
pH	11			3.5			3.5					
NaOCl,kg/h		0.05										
HCl,kg/h			3.7						2.7			2.7
Na_2SO_3,kg/h					0.3							
NaCl,kg/h										3.5		3.5
H_2O,kg/h											5.5	

TABLE 1 Costs of brine purification through precipitation

Product: Purified brine by electrolysis
By-products:
Plant Capacity: 333 m^3/h
Annual production: 2,800,000 m^3
Location:
Depreciation period (years): 10

Process: Precipitation
Fixed capital: 320 Mpta
Working capital:
Operating days/yr: 350
Year used for costing purposes: 1979

Costs items	Unit used in costing	Factor cost unit Ptas	Unit required per m^3 of product	cost pta/m^3 of prod.
VARIABLE COSTS				
Raw materials (minus by-product credits)				
Na_2CO_3	kg	9	0.32	2.88
NaOH	kg	8	0.32	2.56
Energy (minus energy credits)	GJ (MJ)	417	0.03	12.51
Water	m^3			
Labour				
(a) operating	man-hour	700	0.003	2.10
(b) maintenance	man-hour	700	0.0003	0.21
overhead	10% of labour cost			
Miscellaneous				
TOTAL VAR. COST				20.20
FIXED COSTS				
Plant overhead	80% of labour cost	800	0.03 man-hour	2.4
Local taxes and ins.	2% of fixed capital	6.4 Mpta/y	$3.57.10^{-7}$ y/m^3	2.28
Depreciation	10% of fixed capital	32.0 Mpta/y	$3.57.10^{-7}$ y/m^3	11.42
TOTAL PROD. COST				36.36
Return of invest.	% of total capital			
Pollution control				0.99
GRAND TOTAL				37.35

TABLE 2

COSTS OF BRINE PURIFICATION THROUGH EXTRACTION

Product: Purified brine by electrolysis
By-products:
Plant capacity: 333 m^3/h
Annual production: 2,800,000 m^3

Process: Precipitation
Fixed capital: 320 Mpta
Working capital:
Operating days/yr: 350

Location: a/
Depreciation:
Period (year): 10
Year using for costing purposes: 1979

Cost items	Unit used in costing	Factor cost unit pts.	Unit required per m^3 of product	Cost/m^3 of product
VARIABLE COSTS				
Raw materials (minus by-product credits)				
Na_2CO_3	kg.	9	0.32	2.88
NaOH	kg.	8	0.32	2.56
Energy	GJ	417	0.03	12.51
(minus energy credits)	(MJ)			
Water	m^3			
Labour				
(a) operating	man-hour	700	0.003	2.10
(b) maintenance	man-hour	700	0.0003	0.21
overhead	10% of labour cost			
Miscellaneous				
TOTAL VAR. COST				20.20
FIXED COSTS				
Plant overhead	80% of labour cost	800	0.03 man-hour	2.4
Local taxes and ins.	2% of fixed capital	6.4 Mpta/y	$3.57.10^{-7}$ y/m^3	2.28
Depreciation	10% of fixed capital	32.0 Mpta/y	$3.57.10^{-7}$ y/m^3	11.42
TOTAL PROD. COST				36.36
Return of invest.	% of total capital			
Pollution control				0.99
GRAND TOTAL				37.35

a/ Data estimated for the indicated capacity from our plant at Huelva.

TABLE 3

COMPARISON BETWEEN BRINE PURIFICATION THROUGH PRECIPITATION AND THROUGH EXTRACTION

Areas of comparison	Conventional technology	Low- and non-waste technology	Difference
Materials and energy	0.32 kg $NaCO_3/m^3$ 0.32 kg $NaOH/m^3$ 0.03 GJ/m^3	0.7 kg $NaOH/m^3$ 0.7 kg HCl/m^3 2.9 kg H_2O/m^3 2g gas-oil/m^3 0.012 GJ/m^3	Lower variable costs for L/NWT
Generation of waste	3.5kg sludges/m^3 with 92% brine and 20 ppm of Hg	49 l/m^3 brine 30 g Ca/l, 55g Hg/l and 0.3 g Fe/l. pH = 0. No Hg.	No contaminating wastes generated by L/NWT
Pollution control	Sludge treatment and demercurization of water	Not necessary	Fewer process complications and less investment
Waste discharge	Dry cake with 10 ppm Hg and water with 0.01 ppm Hg after treatment	Concentrated chlorides solution 1601/TCl_2	Does not need additional processes to treat the residue (i.e. in L/NWT)
Investment and Production costs	Investment: 320 Mpta. Total cost: 37.35 Pta/m^3	Investment: 303 Mpta. Total cost: 32.56 Pta/m^3	Less investment and costs with L/NWT
Other areas of comparison	see section 7 .6.1.		

. . Additional investment, depending on the treatment consumption for other methods and the degree of purification required varies between 30 and 60 M Pts for the mentioned capacity.

TABLE 4 Cost of demercurizing waste water

Product: Demercurized waste water
By-products: Hg through electrolysis
Plant capacity: $6 m^3/h$
Annual production: $51840\ m^3$
Location: Vilaseca Sabiñanigo
Depreciation period (yr) : 10

Process: MERCUREX
Fixed capital: 25 M pta
Working capital:
Operating days/yr: 360
Year used for costing purposes: 1979

Cost items	Units used in costing	Factor/cost unit pta	Units required per m^3 of residual	Cost/m^3 of residual water
VARIABLE COSTS				
Raw materials (minus by-product credit)				
NaOh	kg	8	0.7	5.60
HCl	kg	6	0.7	4.20
F.Organica	g	0.02	3	0.06
Energy (minus energy credits)	GJ (MJ)	417	0.012	5.00
Water	m	3	0.0029	0.01
Labour				
(a) operating	man-hour	700	0.003	2.10
(b) maintenance overhead	man-hour	700	0.0003	0.21
Miscellaneous				
TOTAL VAR. COST				17.18
FIXED COSTS				
Plant overhead	80% of labour cost	800	0.003 man-hr	2.40
Local taxes and ins.	2% of fixed capital	6.06 M pta/y	$3.57.10^{-7} y/m^3$	2.16
Depreciation	10% of fixed capital	30.3 M pta/y	$3.57.10^{-7} y/m^3$	10.82
TOTAL PROD. COST				32.56
Return on investment	% of total capital			
Pollution control				
GRAND TOTAL				

CREDITS

Hg recovered	kg	283	0.025	7.1
Additional credit	kg	6	3.7	22.2
Acid value of treated water				

UNITED NATIONS

ECONOMIC AND SOCIAL COUNCIL

RESTRICTED

ENV/WP.2/5/Add.19
16 July 1981

ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE
SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

RECOVERY OF DOMESTIC REFUSE (RRR)

Transmitted by the Government of Sweden

1. Identification of industry

Sanitary and similar services. ISIC code[1]: 9200

2. Basic characteristics of production process

The most important methods used at present for processing refuse are incineration, pyrolysis, composting and land-filling. The incineration and the pyrolysis recover the heat in the refuse while composting produces a stable humus which may be employed for soil fertilization. Land-filling gives no recovery at all.

For this comparison incineration has been chosen since it is a rather common method in Sweden. When incinerated, the refuse is reduced to 4 to 10 per cent by volume and produces heat equivalent to 0.2 ton oil/ton refuse if recovered.

3. Name of conventional processing technology

Incineration of domestic refuse.

4. Description of conventional processing technology

4.1 Description of the unit operations/unit processes used in the production process

At an incineration plant the refuse is dumped into a bunker and then conveyed by feeding cranes to the combustion chambers. The residue passes through a feeding chute down onto the firegrate where the residue is burned at a temperature of 950° to 1000°C. The flue gas is then

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex)

effectively mixed and completely burned in the afterburning chamber. At the lower part of the combustion chambers there is a sluice for discharge of the clinker.

The flue gas is cleaned by an electrostatic filter.

The heat from the incineration is recycled as steam which is utilized by nearby industry.

4.2 Specification of materials and energy requirements per ton of input

The energy balance of one ton refuse is:

Energy needed	-29kWh
Energy generated	1543kWh
	1514kWh

This calculation is based on an incineration capacity of 60,000 ton per year and with a refuse calorific value of 2,600 kcal/kg.

4.3 Specification of the form and amount of airborne, waterborne and solid waste generated in the production process

At the incineration plant there is a production of 18,000 tons ash or 30 per cent of the incoming refuse per year. Flue-gas treatment will generate 266 tons of soot or 4.5 per cent of the incoming refuse per year.

4.4 Specification of the emission/effluent/solid waste standard applicable in the reporting country or area

(In Sweden the standard is set by legal procedures before permitting the building or enlargementof industries. The quality of the specific recipient and other local conditions are considered during negotiations)

The temperature in the combustion chamber has to be at least 800°C and the concentration of unburned material in the ash is not allowed to exceed 5 per cent of the weight. The concentration of soot is not allowed to exceed 180 mg/m^3N in the flue gas and the velocity of the flue gas has to exceed 8 m/s.

4.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

The flue gas has to be cleaned by an electrostatic precipitator. (Svenska Fläkt). The gas flow is 136,000 m^3/h with a temperature of 260°C. The concentration of soot in the vented gas is less than 50 mg/Nm^3.

4.6 Specification of the airborne, waterborne and solid waste discharges into the environment

The electric precipitator produces in this case 0.17 kg dust per ton of refuse with a concentration of contaminants as follows:

Hg	0.06	g/ton refuse
Cd	0.26	"
Pb	7.04	"
Zn	10.7	"
Mn	0.43	"
Cu	0.41	"
Cr	0.19	"
Ni	0.24	"

The gas concentration is :

SO_2-SO_3	1.36	kg/ton refuse
NO_x	2.0	"
HF	0.04	"
HCL	3.0	"
Hg	0.003	(steam)

4.7 Cost-related data intended to permit comparison of low- and non-waste technology with conventional technology

See table attached.

5. Name and state of development of low- and non-waste processing technology

The Fläkt "RRR" (Resources Recovery from Refuse) system Full-scale pilot stage.

6. Description of low- and non-waste processing technology

6.1 Description of the unit operation/unit process used in the production process

The process is divided in three mainstages (Fig 1:)

(a) Front end

(b) Black end

(c) Upgrading

Front end

The domestic refuse is conveyed to a shredder (flail type) where the material is treated before separation in the air classifier. It is important that the refuse not be too pulverized so that pieces of metal and glass do not get mixed into the lighter fractions (paper). The shredder consists of two countercurrent rotors with a number of multi-hinged and relatively light-weight beaters.

The material must be in pieces of fairly uniform size and the shredder is therefore combined with a rotation trommel-screen, which completes the process by tumbling and also separates the excessively large items, e.g., plastic film and textiles. The screen consists of a rotating , slightly inclined, perforated drum made of steel plate. A valuable feature of the rotating trommel screen is its buffer action.

In the air classifier, which is of the vertical type with a zig-zag shape, a rising air stream of controlled velocity transports the lighter fractions upwards, whereas heavier material falls through the air stream to the bottom. Differences in the settling rate are thus exploited. In the bottom area, air is introduced at high velocity through a slot. Any light materials adhering to the heavy material is blown away and transferred to the light fraction.

Closed-circuit air circulation is employed and only a small proportion (~10%) of the circulating air is discharged and filtrated. The power supplied to the fan and converted to heat is thus also utilized to create a certain drying effect. Due to the selected air velocity, the light fraction consists predominately of paper, plastic and light vegetable remnants.

The heavy fraction falls on to a conveyor above which a magnet (Magnet Belt Separator) separates ferrous metals in the usual manner. The non-magnetic part of the heavy fraction, undergoes no further treatment, but its energy can be used in connection with incineration.

The secondary shredder is designed to reduce the particle size of the light fraction from the air classifier and has a twofold function. The entrained impurities are liberated and the particle size is more uniform and better suited to further treatment. The shredder is of the impact type with light, hinged beaters on two rotors. Stationary shredding combs are located so that the beater passes between them, thus providing a self clearing effect.

The function of the secondary trommel screen is to remove fine impurities from the paper. The secondary trommel screen is equipped with a fine screening section, to separate material with a particle size less than 15 mm, and a coarse section with 100 mm diameter holes. The fine material consists of particulate food waste which is sufficiently fine to be entrained with the light fraction. The intermediate product, consisting of paper particles between 15 and 100 mm in size, is conveyed pneumatically to the "back end". The waste obtained during fine screening is of interest for composting and the reject obtained after the trommel consists predominantly of plastic film, some paper and textiles.

Back end

The purpose of the back end is to carry out further purification of the paper product and to render it biologically stable, so that it can be stored, transported and handled.

The humid mixture of various types of paper become dried by a flash dryer. The heat supplied to the dryer is obtained from a gas-fired furnace. Because of the thermal economy and other concentrations, the dryer is divided into two stages. In the first stage, the material is dried and the humid drying air is then discharged. In the second stage, the material is heat-treated. The hot air used for this purpose is dry and can be recycled to the process. The function of the heat treatment in the second stage is to kill most of the bacteria in the paper. This takes place by a short thermal shock lasting about five seconds at a temperature between 130°C and 150°C. This treatment involves a compromise, since a higher temperature provides better sterilization but also an undesirable embrittlement of the paper fibres.

Upgrading

The upgrading equipment is basically intended to divide the recycled products into various fractions and to reduce further the loading and wear on the screening equipment of paper mills.

In a vertical air classifier placed after the fresh dryer, mechanical fibres are separated from chemical fibres by exploiting the difference in volume-weight between the two substances as the product is dried. Mechanical fibres are predominant in lighter grades (newspaper), whereas chemical fibres represent a larger proportion of heavier packaging materials (sacks, corrugated board).

In the air classifier, the remaining impurities, predominantly dust, are entrained with and follow the light grades. Therefore, the light product will be further cleaned late in a trommel screen equipped with a fine net instead of holes.

6.2 Specification of materials and energy requirement per ton of input material

The recovery process produces several products which are listed below:

	kg produced material per 1000 kg incoming refuse
Paper	350 kg (100 per cent dry)
Steel	50 kg
Plastic film	65 kg
Compost material	240 kg
Miscellaneous	295 kg

Energy

The plant consumes energy in two forms: mechanical (electric power) and thermal (gas).

Electrical energy

The large electric power consumers, in order of magnitude are:

Primary and secondary shredders

Fans

Conveyors

Miscellaneous

The plant, with a nominal capacity of 5 tons of refuse per hour, has a power demand of about 200 kW or 40 kWh/ton.

Thermal energy

Heat is consumed in the dryer for evaporating water. Part of the heat is recovered by a two-stage procedure, although part of the heat is lost with the hot air discharged into the atmosphere. The heat consumption is 150 kWh/ton of refuse with a paper content of 45 per cent and with the moisture content of the paper being 20 per cent. The total energy consumption is therefore 190 kWh/ton.

6.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

In the recovery process there is a production of coarse residue which consists of a mixture of everything conceivable in domestic refuse. The major components are crusted glass, food residues, gravel, textiles and heavier plastics. The amount of residue is 285 kg per 1000 kg incoming raw refuse. The fabric collector produces an amount of 10 tons dust per year or 0.17 kg dust/ton incoming residue.

6.4 Specification of the emission/effluent/solid waste standards applicable in Sweden

In this area the dust from the fabric collector may not exceed 50 mg/m^3 outgoing air. The generated noise (dB(A)) may not exceed 40 dB(A) at night and 5I dB(A) during the day.

6.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

The air from the air-classifier is cleaned by a fabric collector (Optipulse (Fläkt)) which has a capacity of 40,000 m^3/h and a maximum output of 50 mg dust/m^3. The air is cleaned by a battery of textile filters and the cleaning of the filter itself is done by a pressurized air pulse which is controlled electronically.

6.6 Specification of the airborne, waterborne and solid waste discharges into the environment

Heat is consumed in the dryer for evaporating water. Part of the heat is recovered by a two-stage procedure, although part of the heat is lost with the hot air discharged into the atmosphere. The heat consumption is 150 kWh/ton of refuse.

6.7 Cost-related data intended to permit comparison of low- and non-waste technology with conventional technology

See table attached

APPENDIX 1

Products	Quality (ton)	Price SKr/ton	10^3 SKr
Paper, light	15 000	160	2 400
Paper, heavy	6 000	120	720
Plastic	3 900	240	940
Ferrous metal	3 000	100	300
Organic fine residue	14 400	30[a]	430
Heavy residue	13 200	-	-
(Water)	(4 500)	-	-
Refuse	60 000		4 790
Income per ton of refuse:		SKr	80
		(1979) US $	19.00

Composted [a]

APPENDIX 2

Energy savings when recovered materials are used instead of virgin raw materials.

Material	Energy savings kWh/ton (heat content)
paper	2 000
plastic	10 000
ferrous metal	2 500

Average value (50% electricity) 0.015 $/kWh

7. Schematic comparison between the conventional and the low- and non-waste technology

Areas for comparison	Conventional technology	Low- and non-waste technology	Difference (b)-(a)
Materials	60,000 tons refuse	60,000 tons refuse	-
Energy-consumption	154 kWh/ton	190 kWh/ton	+36 kWh/ton
Energy-production	1540 kWh/ton	1475 kWh/ton a/	-65 kWh/ton
Recycled material tons/year	-	paper 21 000 iron 3 000 plastic 3 900 compost 14 400	
Waste kg/ton income refuse	Ash 265 Soot 4.5	Coarse residue 235 Dust 0.2	+20 -4.3
Investment costs US $	4.0 million (1962-1976)	7.9 million (1979)	
Total costs US $/ton	26.70 (1979)	27.00 (1979)	+0.30
Revenues US $/ton	16	19 (41) b/	+3.0 (+25.00) b/
Net US $/ton	10.70	8 (1979) (-14) b/	-2.70 (-24.70) b/

---

a/ Indirectly via recycling of recovered material. See appendix 2

b/ Including value of energy savings when recovered materials are recycled

8. Identification of needs for further research and development with regard to low- and non-waste technology

The calculations made above are based on the assumption that markets can be found for the recovered materials. The reclaimed paper fraction has been tested and found to be feasible as raw materials in today's manufacture of cardboard, replacing recovered newspaper. It should, however, be possible to widen the range of useful areas, which is an important task for further development.

Mechanical sorting makes it possible to recover a higher percentage of waste paper than would be obtained with source separation in the household. It is, however, a matter of putting the recovered fibre to a suitable use, such as for products in which the quality requirements can be met, thereby saving original fibre sources for more qualified purposes.

9. Reporting organization

AB Svenska Fläktfabriken
Pack
S-104 60 Stockholm
Sweden

10. Date of report

23 November 1979

4.7 Cost-related data intended to permit comparison of low- and non-waste technology with conventional technology

Product: Household waste
By products: Steam
Plant capacity: 95,000 ton waste
Annual production: 60,000 (1978)

Process:
Fixed capital:$4.0mil
Working capital:$4.0mil
Operating days/yr: 245

Location: Uppsala
Depreciation: 15 year 10% interest
Year used for costing purposes: 1978

Cost items	Units used in costing	Factor/cost unit	Units required per ton of product	Cost/ton of product ($)
VARIABLE COSTS				
Raw materials (minus by product credits)		60,000 tons household waste 140,440 tons steam = 0.01 $/kWh	1 ton/ton 2.38 ton a/ton = 1.54 MWh/ton	-16.00[a]
Energy (minus energy credits)	GJ (MJ)	0.022 $/kWh electricity 0.016 $/kWh heating	0.0588 MWh/ton 0.0968 MWh/ton	1.30 1.60
Water	m^3	0.625 $\$/m^3$	0.160 m^3/ton	0.10
Labour				
(a) Operating	man-hr	12 $/h	0.455 h/ton	5.50
(b) Maintenance	man-hr		0.131 h/ton	1.50
overhead	% of labour	18.4 % of (a)+(b)	1.30 $/ton	1.30
Miscellaneous				0.50
TOTAL VAR; COST				-4.20
FIXED COSTS				
Plant overhead	% of labour costs	77.8% of (a)+(b)	5.40 $/ton	5.40
Local taxes and ins.	% of fixed capital	0.59	0.40 $/ton	0.40
Depreciation and interest	% of fixed capital		6.70 $/ton	6.70
TOTAL PROD. COST				8.30[a]
Return on investment	% of total capital	-	-	-
Pollution control		-	-	-
GRAND TOTAL				8.30[a]

---

[a] Not including capital costs for heat distribution systems

6.7 Cost-related data intended to permit comparison of low- and non-waste technology with conventional technology

Product: See appendix
Byproducts: -
Plant capacity: 60,000 tons/year
Annual production: 60,000 tons/year

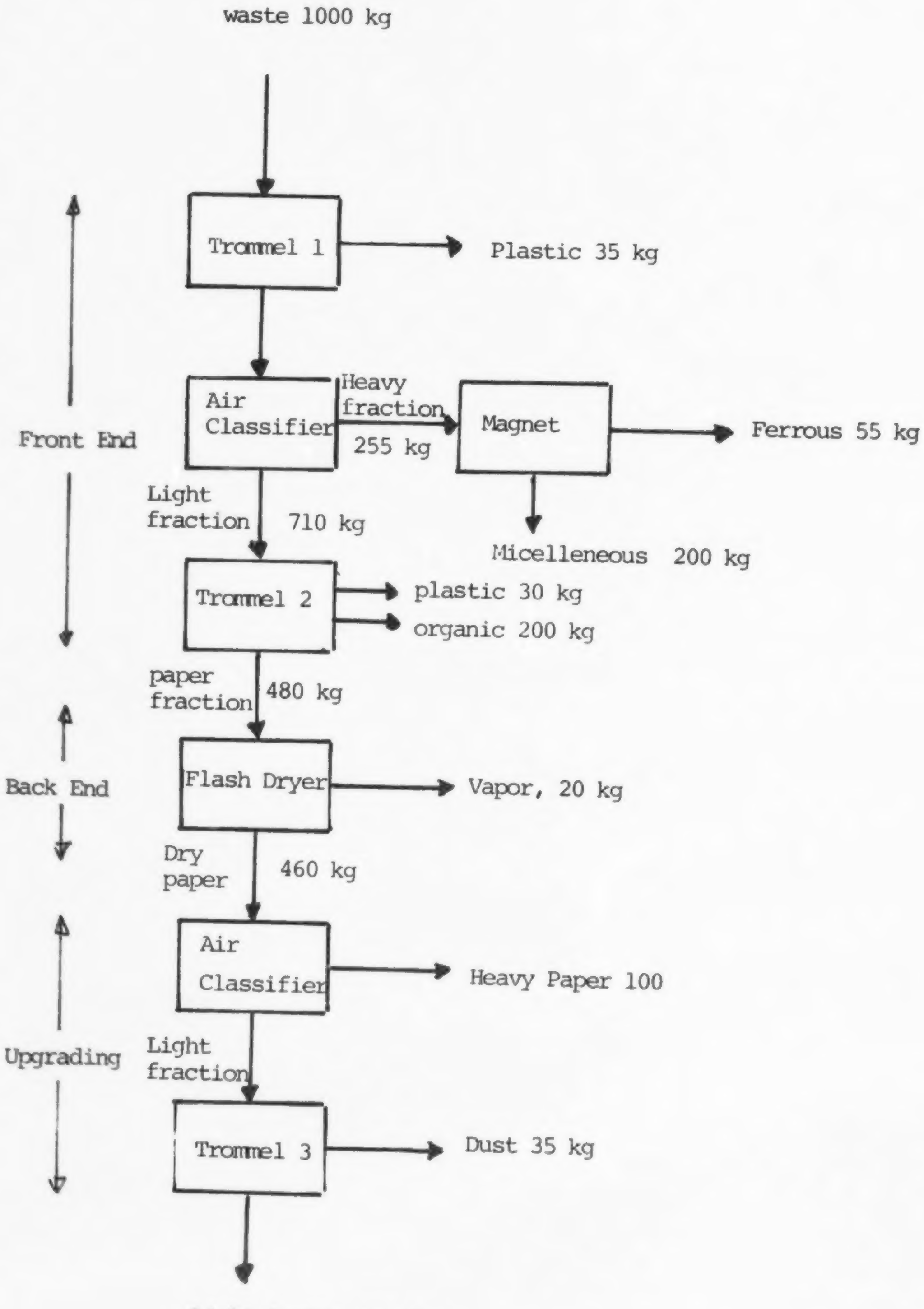
Process: Dry mechanical recovery of household waste
Fixed capital: $7.85 mil
Working capital: $7.85 mil
Operating days/yr: 250 d/y

Location: Sweden
Depreciation: 10 year machinery
20 year building
10% interest
Year used for costing purposes: 1979

Cost items	Units used in costing	Factor/cost unit	Units required per ton of prod.	Cost/ton of product ($)
VARIABLE COSTS				
Raw materials (minus by-product credits)	-	See appendix	-	-19.00
Energy (minus energy credits	GJ (MJ)	Electric: 0.022 $/kWh	40 kWh/ton a/	+ 0.90
		Thermal: 0.016 $/kWh	150 kWh/ton a/	+ 2.40
Water	m^3			
Labour				
(a) Operating	man-hr	45 SKr/man-hr including social-cost	15 men/shift 1/3 man-hr/ton	+ 3.60
(b) Maintenance overhead	man-hr % of labour cost			+ 2.10
Miscellaneous				
TOTAL VAR. COST				-10.00
FIXED COSTS				
Plant overhead	% of labour costs	-	-	
Local taxes and insurance	% of fixed capital	-	-	
Depreciation and interest	% of fixed capital			+18.00
TOTAL PROD. COST				+ 8.00
Return on investment	% of total capital			
Pollution control	included in machinery			-
GRAND TOTAL				+ 8.00

a/ Not including energy credits when recovered materials are recycled see appendix 2

Fig 1. Flow diagram of the RRR-system


waste 1000 kg
Trommel 1
Plastic 35 kg
Front End
Air Classifier
Heavy fraction
255 kg
Magnet
Ferrous 55 kg
Micelleneous 200 kg
Light fraction
710 kg
Trommel 2
plastic 30 kg
organic 200 kg
paper fraction
480 kg
Back End
Flash Dryer
Vapor, 20 kg
Dry paper
460 kg
Air Classifier
Heavy Paper 100
Upgrading
Light fraction
Trommel 3
Dust 35 kg
Light Paper 325 kg

UNITED NATIONS

ECONOMIC
AND
SOCIAL COUNCIL

E

RESTRICTED

ENV/WP.2/5/Add.20
23 July 1981
ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

SENIOR ADVISERS TO ECE GOVERNMENTS
ON ENVIRONMENTAL PROBLEMS

Working Party on Low- and Non-Waste
Technology and Re-utilization and
Recycling of Wastes

COMPENDIUM ON LOW- AND NON-WASTE TECHNOLOGY

Monograph

SMELTING REDUCTION OF NON-AGGLOMERATED IRON ORE CONCENTRATES USING LOW-GRADE COAL AS THE SINGLE SOURCE OF ENERGY (INRED PROCESS)

Transmitted by the Government of Sweden

1. Identification of industry

Iron and steel industry (Raw iron manufacturing).
ISIC code [1]: 3710

2. Basic characteristics of production process

Reduction of iron oxides contained in iron ore agglomerates and melting of metallic iron.

3. Name of conventional processing technology

Blast furnace process.

4. Description of conventional processing technology

4.1 Description of the unit operations/unit processes used in the production process

The transformation of iron ore into raw iron takes place in a series of distinctly different processing steps. The three principal steps are:

(a) Preparation of raw materials;

(b) Coke-making; and

(c) Raw iron manufacturing

The first processing step of raw iron manufacturing can be divided into two sub-processes, namely:

---

[1] International Standard Industrial Classification of All Economic Activities (ENV/WP.2/5/Annex).

(a) ore preparation (which is generally carried out at the mine); and

(b) sintering or pelleting.

In the sintering process, the fine ore particles are agglomerated into a porous mass that is suitable to be charged into the blast furnace. The purpose of the sintering is, apart from an agglomeration of the ore concentrate, to burn some of the sulphur compounds contained in the ore concentrate. The sintering machine is charged with a mixture of iron ore concentrate, coke dust, and limestone which is lit by gas flames. In order to obtain the high temperature necessary for the agglomeration to take place, air is sucked through the mixture with the help of large fans.

The coke, which serves as fuel and reactive agent in the raw iron manufacturing process (i.e. in the blast furnace), is produced by treating metallurgical coal in the absence of air to a temperature at which the major part of the non-carbon components of the coal (i.e. volatile matter, water and sulphur) are driven off. Since approximately 25 per cent of the coal is carburated during the coking process, large amounts of coke-oven gas are generated. In the most common method of coke manufacturing, the by-product coking process, the coke-oven gas is treated in order to recover by-products like tar, ammonia, sulphur, light oil, and phenol. The treated coke-oven gas is either used as fuel elsewhere in the iron and steel plant, sold as town gas or flared off.

The primary inputs to the process of raw iron manufacturing are sinter (or pellets) and coke. Lump iron ore is sometimes also used. Each ton of raw iron requires approximately 1.6 tons of sinter or pellets. Sinter, pellets and iron ore contain iron primarily in the form of iron oxide and in order to get raw iron, the iron oxide must be reduced. This reduction is accomplished under high temperature in the blast furnace. In order to attain the high temperature necessary for the reduction of the iron oxide and the melting of the metallic iron, pressurized hot air is injected at the bottom of the furnace.

When the air (preheated to approximately 1,000°C) is blown through the furnace from the bottom, the coke burns and forms carbon monoxide which passes through the furnace. This carbon monoxide is the active agent in the process since it can combine with oxygen. Most of the carbon monoxide generated combines with the oxygen of the iron oxide and forms carbon dioxide. The gas leaving the top of the blast furnace consists of carbon monoxide (25 to 30 per cent), carbon dioxide (17 to 19 per cent),, hydrogen (1 per cent) and nitrogen (58 per cent). Since this combustible gas has a high load of particulates, it must be cleaned before it can be used as fuel elsewhere in the plant. Cleaning of the blast furnace gas is therefore considered a normal part of the raw iron manufacturing process.

One of the major impurities in the iron ore (and in the coke) is silica (SiO_2). This mineral has a very high melting point and if some method of removing the silica from the furnace were not provided, the furnace would rapidly fill up with ashes and become inoperative. This problem is prevented by the addition of limestone as, at the high temperature of the furnace, the lime combines with the silica to form a low melting material called slag. The molten slag is lighter than the melted iron and, therefore, floats on top of the iron. As the iron is tapped from the bottom of the furnace, the floating slag is skimmed off. Molten iron and slag are drawn off from the furnace five to six times each day. Depending upon its size, a blast furnace will produce from a few hundred to over 10,000 tons of raw iron per day.

4.2 Specification of materials and energy requirements per ton of output

The raw materials and energy requirements per tonof raw iron is shown below:

Raw materials and fuels	kg/t	GJ/t
Iron ore agglomerate (Fe content 65%)	1 540	
Limestone	200	
Coke	420	12.3
Fuel oil	60	2.5
Coke plant underfiring		2.2
Sinter plant coke breeze and gas		3.0
		20.0
Credit for blast furnace gas		-3.4
		16.6
Electrical energy	**kWh/t**	
Blast furnace	100	
Sinter plant	40	
	140	
Recalculated as primary fossil energy (y= 0.35)		1.4
Grand total as primary energy		18.0

4.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

The wastes generated during the sintering process are primarily particulates and sulphur dioxide. The sulphur dioxide is generated in the sintering machine and originates from the sulphur in the iron ore concentrate and the coke dust. If oil is used as fuel in the sintering machine, the amount of sulphur dioxide generated will be correspondingly higher. The range of variation for the raw loads of sulphur dioxide is 1.0 to 12.0 kg/ton of sinter. The particulates generated during the sintering process originate primarily from the sintering machine and from the raw materials and sinter handling stations (together over 80 per cent of particulates generated). The raw loads of particulates generated in the sintering process generally vary between 15 and 25 kg/ton of sinter. Other wastes, such as nitrogen oxides and fluoride could also be present in the emissions from the sintering process.

The coking process generates a number of airborne, waterborne and solid waste products. The principal sources of airborne waste are the coal and coke handling operations, the charging and discharging (pushing) of the coke oven, and the burning of the coke in the ovens. Approximately 70 per cent of the airborne waste (apart from sulphur dioxide) generated at a coke plant, originates from the charging of the ovens. The range of variation for the raw loads of airborne wastes from a coke plant are for particulates 0.5 to 3.5 kg/ton of coke, for sulphur dioxide 0.2 to 5.0 kg/ton, for hydrocarbons 0.2 to 2.0 kg/ton, for hydrogen sulphide 0.1 to 0.8 kg/ton, and for hydrogen cyanide 0.1 to 0.6 kg/ton.

The most significant waterborne residuals generated at a coke plant originate from the coke quenching and from the gas cleaning in the by-product plant. For a coke plant as a whole, the range of variation of the raw loads of some of the major waterborne waste products are as follows: Ammonia 0.3 to 2.0 kg/ton, suspended solids 0.07 to 15.0 kg/ton, phenols 0.3 to 5.0 kg/ton, sulphide 0.3 to 2.5 kg/ton, cyanide 0.15 to 5.0 kg/ton, and BOD_5 0.9 to 6.0 kg/ton.

The practice of cleaning the blast furnace gas means that, under ordinary operating conditions, negligible amounts of airborne waste are emitted through that gas stream. Thus, the only airborne waste products in connection with raw iron manufacturing are the particulates from the lapping operation. The range of variation for the raw load of this waste product is 0.2 to 1.6 kg/ton.

The water used for gas cleaning purposes generally contains 0.8 to 5.0 kg/ton of suspended solids, 0.3 to 0.4 kg/ton of sulphide, 0.1 to 0.2 kg/ton of ammonia, less than 0.1 kg/ton of fluoride and less than 0.05 kg/ton of cyanide and phenol. The pH of the gas cleaning water ranges between 7 and 9.

The large quantity of slag produced in the blast furnace (1200 to 2400 kg/ton) is generally granulated before final disposal. The water used in connection with slag granulation is also contaminated with suspended solids and various chemical compounds. The amount of suspended solids varies between 1 and 2 kg/ton of raw iron and the amount of chlorides between 0.3 and 0.9 kg/ton. The water generally also contains between 0.3 and 0.4 kg/ton of sulphates and less than 0.1 kg/ton of hydrogen sulphide.

Since blast furnaces are generally quite large and operate at high temperatures, large volumes of cooling water are normally required. Most plants use once-through cooling systems, although recirculation of cooling water is practiced in some areas with limited water supplies. The temperature rise of the cooling water is quite moderate, however, and rarely exceeds 5°C.

Since dry cyclones are generally used as a first step in the gas cleaning process, 20 to 30 kg particulates per ton of raw iron are generated as dry solid waste.

4.4 Specification of the emission/effluent/solid waste standards applicable in Sweden

Swedish environmental policy is based on a plant-by-plant determination of permissible discharges rather than on national emission standards.

4.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

The airborne wastes associated with sinter plant operation are primarily: (a) particulates that become entrained in the combustion air as it is drawn through the sinter mixture into the windbox; (b) particulates occurring due to the transportation of the sinter during the cooling operation; and (c) particulates that are generated during the crushing and screening operations.

The sulphur contained in the fuel (oil and gas for firing and coke) is generally not considered to be a problem, since on the average only about 55 kg of fuel are needed to produce one ton net of sinter. However, certain iron ores have high sulphur content which would result in high sulphur oxides emissions. Oil and grease, which are volatilized from recycled materials, and the vaporization of certain metallic components cause emissions of hydrocarbons and smoke that are difficult to control.

All sinter plants use dry cyclones for "primary" control of particulate emissions. For "secondary" control, plants built today are generally equipped with high-efficiency cyclones or fabric filters in order to minimize power costs and to avoid the problems inherent the disposal of the effluents generated by a wet particulate control system.

In the coke-making process, the unloading, stockpiling and reclamation of coal cause fugitive emissions of particulates which are difficult to control. The most commonly used method has been to enclose the conveyors, screens and other handling equipment then vent the dust-laiden air from these operations through a particulate removal system such as a fabric filter. The particulates collected during these operations are generally returned to the storage bunkers for pulverized coal.

With regard to particulate emissions during the coke-oven charging operation, there are basically only two methods of control, both related to the design and operation of the process. One involves the use of increased suction in the collector main, combined with a charging procedure called "sequence charging"; the second employs lorry cars with a self-contained scrubber system. A third method of reducing particulate and gaseous emissions during charging, called "pipeline charging", is just coming into industrial use.

During the coking cycle, gaseous emissions can escape from the ovens through the charging ports and end doors. Controlling emissions from the charging ports is basically a matter of properly sealing the lids and sealing them with refractory slurries. To a certain extent, therefore, the leakage of gases around the oven doors is a matter of good maintainance.

When the coke is discharged (pushed) from the coke-oven, convection currents carry off the dust from the coke. If there is uncoked material in the oven, combustion of its volatile components will create gaseous emissions.

One method of control is the use of oven side shed enclosures, which permits the capture of side-door leakage. However, considerable energy is needed to provide adequate ventilation; artificial lighting is required; any initial investment cost is high. There are also certain occupational safety and health problems associated with this method. A second alternative is the use of mobile bench-mounted, self-contained hoods that include dusting, a wet scrubber and fans. Other alternatives include self-contained hooded quench-cars with integral scrubbers and fixed collection hoods extending the full length of a battery.

Many of these devices are difficult to apply to older ovens. Mobile versions, for example, require redesign of the bench and coke-car tracks, while others are designed to be used in conjunction with new, emissions-reducing quenching methods.

Coke-oven side hoods and mobile hot-car enclosures (both equipped with, or being connected to, gas cleaning systems) are presently being tried on commercially operating ovens.

The most common method of controlling particulate emissions from the quenching of the coke, is to install baffles in the quench tower. However, baffles will only remove heavier particles from the gas stream and small amounts of fine particles are carried off with the plume. In order to minimize emissions of objectionable organic vapours, clean water can be used for quenching. An even more effective way to reduce emissions from the quenching operation is to use a continuous enclosed quenching system in conjunction with hooded coke cars.

The principal gaseous emissions from the coking process are hydrogen sulphide in the coke-oven gas and sulphur dioxide in the products of combustion. The approach taken by most plants has been to try to reduce the concentration of hydrogen sulphide in the coke-oven gas rather than to treat the flue gas. Installations for reducing the emissions of hydrogen sulphide are constructed on the basis of modules capable of handling large amounts of coke-oven gas per day. The use of multiple modules is a common practice used to guard against complete failure in the case of operating disruptions. In order to reduce sulphur dioxide emissions, it would be necessary to install equipment for flue-gas desulphurization.

The principal sources of waterborne wastes from coke plants are the quenching operation and the processes that clean and recover chemicals from the coke-oven gases.

The most widely practised methods for treatment of coke plant effluents are:

(a) ammonia liquor treatment via free ammonia still;
(b) dephenolization;
(c) sedimentation of suspended solids in settling ponds;
(d) light oil recovery;
(e) recycling of quench water without blowdown;
(f) recycling of final cooler water with blowdown to dephenolizer;
(g) benzol plant wastes blowdown to dephenolizer; and
(h) sedimentation of once-through crystallizer water.

Common to all operations included in the treatment measures listed above is that they require constant attention regarding maintenance and housekeeping and that very close control of intermediate steps must be practised.

Since cleaning of blast furnace gas is a normal part of the raw iron manufacturing process, the cleaning costs are regarded as ordinary operating expenses rather than pollution control costs. Thus, the only airborne wastes that are generated in the raw iron manufacturing process are the particulates originating from the handling of material in the stock house, the kish (fine graphite) that is evolved from the iron as it flows from the blast furnace slag in the presence of moisture and the fugitive emissions from the cast house and slag piles.

In order to be able to use the blast furnace gas as fuel, it is first passed through a settling chamber (dust catcher) to allow dust particles to precipitate out. Since this is a dry operation, no effluents result. Following the dust catcher, the gas is normally passed through wet scrubbers and coolers. In some instances, all or part of the gas is also passed through electrostatic precipitators for further cleaning. It is the effluent from the gas scrubbers and cooler that contains the major portion of the waterborne wastes originating from the blast furnace operations.

The coke delivered to the blast furnace generally contains a certain amount of phenol and nitrogen compounds. The concentration of these materials in the coke can be quite high, especially if the coke has been quenched with one of the coke plant's waste-water streams. These compounds evaporate from the coke in the top of the blast furnace and leave the furnace with the blast furnace gas. A certain portion of these compounds, along with the cyanide formed, is transferred to the water during the cleaning of the gas in the scrubbers.

There are presently two common processes for handling the slag drawn off the blast furnaces. These processes are (a) air cooling, and (b) slag granulation.

In the process of air cooling, the molten slag is poured into dry pits for slow cooling. A limited amount of water is sprayed on the hot slag in order to accelerate the cooling. The slag slowly solidifies into one solid mass in the pit and is subsequently dug out with a power shovel. Most of the water sprayed on the hot slag evaporates, but if the sprays are not properly controlled and excessive amounts of water are used, a contaminated liquid is drained from the pit.

In the granulation process, slag is usually run into a pit of water adjacent to the furnace. High pressure streams of water disassociate the column of liquid slag as it falls into the pit. This rapid cooling forces the slag to expand and crack into small particles. This process generates large amounts of steam with a slight odour of hydrogen sulphide. Granulated slag is quite light and some of the particles tend to float on the granulation water. The use of this process has declined in recent years to some extent because of the difficulty of keeping the floating slag particles out of the receiving waters and problems of odours caused by the steam plume.

4.6 Specification of the airborne, waterborne and solid waste discharges into the environment

(a) Sintering Plant

In order to follow Swedish guidelines for particulate emissions from sintering plants of 1.0 kg/ton of sinter, particulate removal efficiency has been increased to approximately 95 per cent. There is no flue-gas desulphurization.

(b) Coke plant	kg/t of coke (range)
Particulates	0.04-0.25
Sulphur dioxide	0.01-0.35
Hydrocarbons	0.01-0.06
Hydrogen sulphide	0.01-0.06
Hydrogen cyanide	0.01-0.04

Ammonia	0.02-0.13
Phenol	... -0.02
Cyanide	... -0.05
BOD_5	0.07-0.5
Sulphide	... -0.01
Oil and grease	<0.03
Suspended solids	0.04-3.34

(c) Blast furnace	kg/t of iron (range)
Particulates	0.2 -1.6
Gas cleaning water	
Ammonia	0.04-0.08
Phenol	< 0.01
Cyanide	<0.01
Sulphide	...
Suspended solids	< 0.01
Fluorine	< 0.03
Slag granulation water	
Chloride	0.04-0.1
Hydrogen sulphide	...
Sulphate	...
Suspended solids	...

4.7 Cost-related data intended to permit comparison of low- and non-waste technology with conventional technology

For a blast furnace with a capacity of 500,000 tons of raw iron per year (including sinter plant and facilities for raw materials handling), investment costs would amount to approximately US$ 260/ton of capacity. In this size range it is more economical to buy coke on the market than to invest in a coke plant.

The pollution control measures requried for such a plant (excluding desulphurization of sinter plant waste gas) would necessitate investments of between US$ 15 and 27 depending upon the specific emission/effluent standards applied to the plant. Thus, pollution control measures would account for between 5.8 and 10.5 per cent of total investment costs for the plant. This corresponds quite well to the findings of a recent OECD study, which estimated this range to be 7 to 10 per cent.[2] A specification of unit production costs is presented in Table 1.

---

[2] Emission Control Costs in the Iron and Steel Industry. Organization for Economic Co-operation and Development, Paris, 1979.

5. Name and state of development of low- and non-waste technology

Intensive reduction of non-agglomerated iron ore concentrates using low grade coal as the single source of energy (INRED-process). A pilot plant producing 3 to 5 tons of raw iron per hour is in operation.

6. Description of low- and non-waste technology

6.1 Description of the unit operations/unit processes used in the production process

Fine-grain iron ore concentrates and other iron oxides are smelted without any kind of agglomeration. The only source of energy is coal which is fed into the smelting furnace together with the iron ore concentrates. A schematic flow diagram of the process is presented in Figure 1.

The reduction takes place in a single reactor (Figure 2) starting with flash smelting of the concentrate by coal and oxygen in the upper part of the reactor. The ore is prereduced to FeO and the charge is superheated. Close to 90 per cent of the process energy is supplied in this step. Final treatment then follows in a furnace forming the lower part of the reactor. Here, the remaining need for energy is supplied in the form of electricity via electrodes. Hot metal and slag collects in the bottom and are lapped at intervals.

The combustion of the coal is controlled in order to produce an amount of coke that is sufficient for final reduction and carburization of the iron in the electric furnace (i.e. the lower part of the reactor).

The completely burned-out gases from the reactor are cooled in an adjacent waste heat boiler. Steam produced in the boiler and in the cooled flash-smelting chamber will in the standard case be utilized in a condensing turbine to generate power for the oxygen plant compressor and the electricity generator for the furnace. For practical reasons the plant will be connected to the grid.

If low pressure steam can be utilized, it might be advantageous to use a back pressure turbine and to buy supplementary electrical energy from the grid. Schematic illustrations of the energy balance of the process are presented in Figures 3 and 4.

6.2 Specification of materials and energy requirements per ton of output

The requirements of materials and energy per ton of raw iron is as follows:

	kg/t	GJ/t
Iron ore (iron content 65%)	1,540	
Limestone	230	
Coal (ash content 16%, dry weight)	600	17.2

CASE 1 - Condensing turbine:

No electricity bought	-
Grand total, case 1	17.2

CASE 2 - Back pressure turbine:

330 kWh bought electricity, (expressed as primary fossil fuel $\eta=0.35$)	3.4
Credit for back pressure stream	-5.7
Grand total, case 2	14.9

6.3 Specification of the form and amount of airborne, waterborne and solid wastes generated in the production process

In the INRED-process, the following waste products are generated:

- Slag, around 330 kg/ton (The slag is of a blast-furnace nature and could be utilized)
- Waste gas, approximately 1,500 Nm^3/ton
- Cooling water, from power plant condensor, from the cooler of the compressed air supplied to the oxygen plant, and from the INRED-reactor
- Dust from the flash smelting (around 150 kg/ton is recycled)
- Dust bled off in order to create an outlet for lead, zinc and alkalines. (The amount depends on the concentrations of these elements but is typically around 20 kg/ton).

6.4 Specifications of the emission/effluent/solid waste standards applicable in Sweden

See subsection 4.4

6.5 Specification of (add-on) pollution control measures necessary for compliance with existing standards

The waste gas is cleaned in cyclones and an electrostatic precipitator in order to reduce particulate emissions and to recover dust which can be recycled. As pointed out above, part of the dust can be recycled. The bled-off dust together with dust from steel-making furnaces, etc., may be pressed batch-wise, or continuously in a separate INRED-unit, in order to concentrate the lead and zinc contained in the dust into marketable products.

Depending on local regulations, "add-on" equipment for removal of sulphur dioxide in the waste gas may be required. Pollution control equipment of the "add-on" type will also be needed in order to control particulate emissions from tapping and handling of iron and slag.

6.6 Specifications of the airborne, waterborne and solid waste discharges into the environment

- Waste gas, 1500 Nm^3/ton (cleaned according to standards laid down in permit for plant).
- Heat in waste gas;
- Cooling water, heat content around 5 GJ/ton
  (If back pressure turbine is used) 0.9 GJ/ton
- Slag, heat content 0.6 GJ/ton
- In the case of SO_2 - removal, sludge from gas scrubber.

6.7 Cost-related data intended to permit comparison of low. and non-waste technology with conventional technology

The investment costs for a 350,000 tons/year INRED-plant including oxygen plant, power station, and facilities for handling of raw materials can be estimated at around US$ 186 per ton of annual capacity. This sum does not include equipment for removal of sulphur dioxide from the waste gas. The cost for such a unit would be around US$ 10 per ton of annual capacity. A specification of the unit production costs of the INRED-process is presented in Table 2.

7. Schematic comparison between the conventional and the low- and non-waste technology

See attached chart.

8. Identification of needs for further research and development with regard to the low- and non-waste technology

The present aim is to build a commercial scale demonstration plant.

9. Reporting organization

Boliden AB
Box 5508
S-114 85 Stockholm
Sweden

10. Date of report

20 September, 1979.

7. Schematic comparison between conventional and low- and non-waste technology

Area for comparison	Conventional technology	Low- and non-waste technology	Difference
Energy	GJ/t	GJ/t	
Counted as primary fossil energy	18.0	Type of turbine: Condensing 17.2 Back pressure 14.9	Saving 0.8 GJ/t or 4% 3.1 GJ/t
Investment cost			
Capacity t/y	500 000	350 000	74 US$/t/y
US$ t/y	260	186	
Unit production cost			
Variable cost	122.2	91.6	
Plant overhead	3.9	4.0	
Depreciation 15%	41.9	30.1	
Total	168.0	125.7	42.3 US$/t

Waste discharges

Conventional technology: Waste gas from coke plant, sinter plant and blast furnace stoves. Sludge from blast furnace wet gas cleaning.

Low- and non-waste technology: Waste gas only from the reactor. Bled off dust from gas-cleaning may be upgraded and regarded as non-waste containing zinc and lead.

Pollution control measures

Conventional technology: The coke plant raises the most difficult problems in the steel industry. The sinter plant also poses problems especially if SO_2- cleaning of the waste gas will be specified in the future. The blast furnace problems are related to the sludge from the gas cleaning and to cyanides in the gas-cleaning water.

Low- and non-waste technology: The process waste gas appears only in one stream, which is of comparatively low volume due to the use of oxygen. This facilitates, inter alia, the removal of SO_2. Cyanides and NO_x in the waste gas are low.

Other areas for comparison

The new technology is able to utilize all kinds of fine grained iron oxide raw materials. The tolerance is high for sulphur, zinc, lead and alkalines. The new technology is also able to utilize low grade coal with high ash and sulphur contents. Coking properties are unimportant.

When producing low phosphorus iron, the toelrance for phosphorus in the coal is higher than in the blast furnace process. The products, hot metal and slag, are of similar grade in both technologies. As in the blast furnace, the INRED furnace allows control of the silicon content within certain limits. Regarding the working environment, the new technology provides a less noisy working place around the furnace. Further, it is an advantage that the working places around the coke ovens and sinter plants are eliminated.

Table 1: Unit Production Cost, Blast furnace-process

Products: Raw iron (Hot Metal)	Process: Blast furnace	Location: Sweden
By-products: Slag	Fixed capital: US$ 130 million	Depreciation: 15% annuity
Plant capacity: 500 000 t/y	Working capital: US$ 10 million	Year used for costing purposes: 1979
Annual production: 465 000 t/y	Operating days/yr: 340	

Cost items	Units used in costing	Factor/cost unit US $	Units required per ton of prod.	Cost/ton of product US$
VARIABLE COSTS				
Raw materials				
Concentrate	ton	25.7	1.54	39.5
Limestone	"	11.0	0.20	2.2
Sintering cost	"	11.9	1.0	11.9
Energy				
Coke	"	123	0.450	55.4
Oil	m^3	116	0.030	3.5
Electricity	kWh	0.035	100	3.5
Credit, gas				-7.0
Labour at Blast Furnace				
Operating	man-hr	13.3	0.29	3.9
Maintenance including relinings				4.0
Miscellaneous				5.3
TOTAL VAR. COST				122.2
FIXED COSTS				
Plant overhead	% of labour costs		100	3.9
Local taxes and ins.	% of fixed capital			-
Depreciation	% of fixed capital		15	41.9
TOTAL PROD. COST				168.0
Return on investment	% of total capital			
Pollution control				
GRAND TOTAL				

Table 2: Unit Production Cost, INRED-process

Products: Raw iron (Hot Metal)
By-products: Slag
Plant capacity: 350 000 t/y
Annual production: 325 000 t/y

Process: INRED
Fixed capital: US$ 65 million
Working capital: US$ 5 million
Operating days/yr: 340

Location: Sweden
Depreciation: 15% annuity
Year used for costing purposes: 1979

Note: Cleaning of waste gas from SO_2 is not included.

Cost items	Units used in costing	Factor/cost unit	Units required per ton of prod.	Cost/ton of product
VARIABLE COSTS				
Raw materials				
Concentrate	ton	25.7	1.54	39.5
Limestone	"	11.0	0.23	2.5
Energy	"			
Coal		53.5	0.60	32.1
Power subscription 5 MW				0.4
Electrodes				2.7
Labour				
Operating	man-hr	13.3	0.36	4.8
Maintenance				4.0
Miscellaneous				5.6
TOTAL VAR. COST				91.6
FIXED COSTS				
Plant overhead	% of labour costs		100	4.0
Local taxes and ins.	% of fixed capital			-
Depreciation	% of fixed capital		15	30.1
TOTAL PROD. COST				125.7
Return on investment	% of total capital			
Pollution control				
GRAND TOTAL				

Fig.1
INRED Function

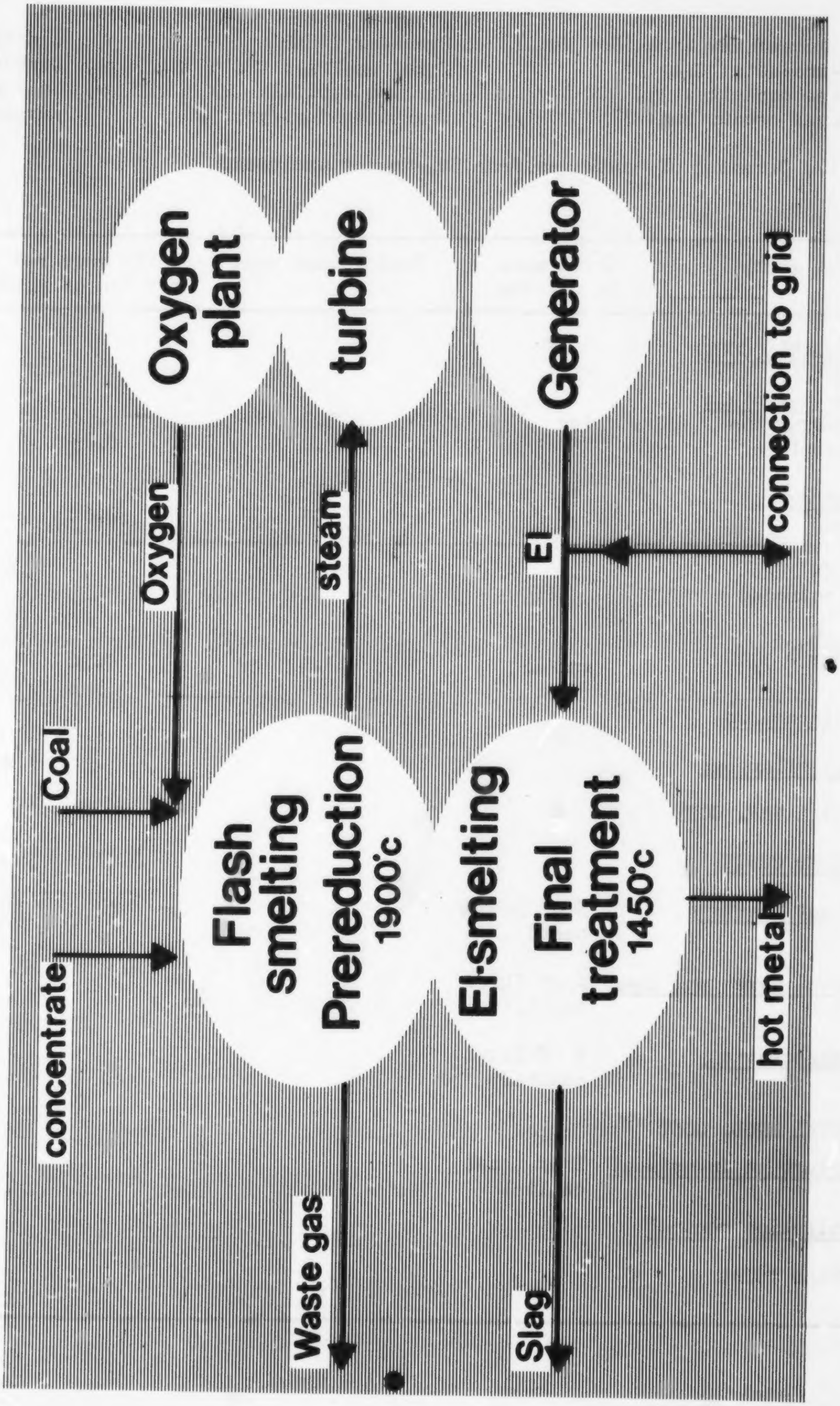
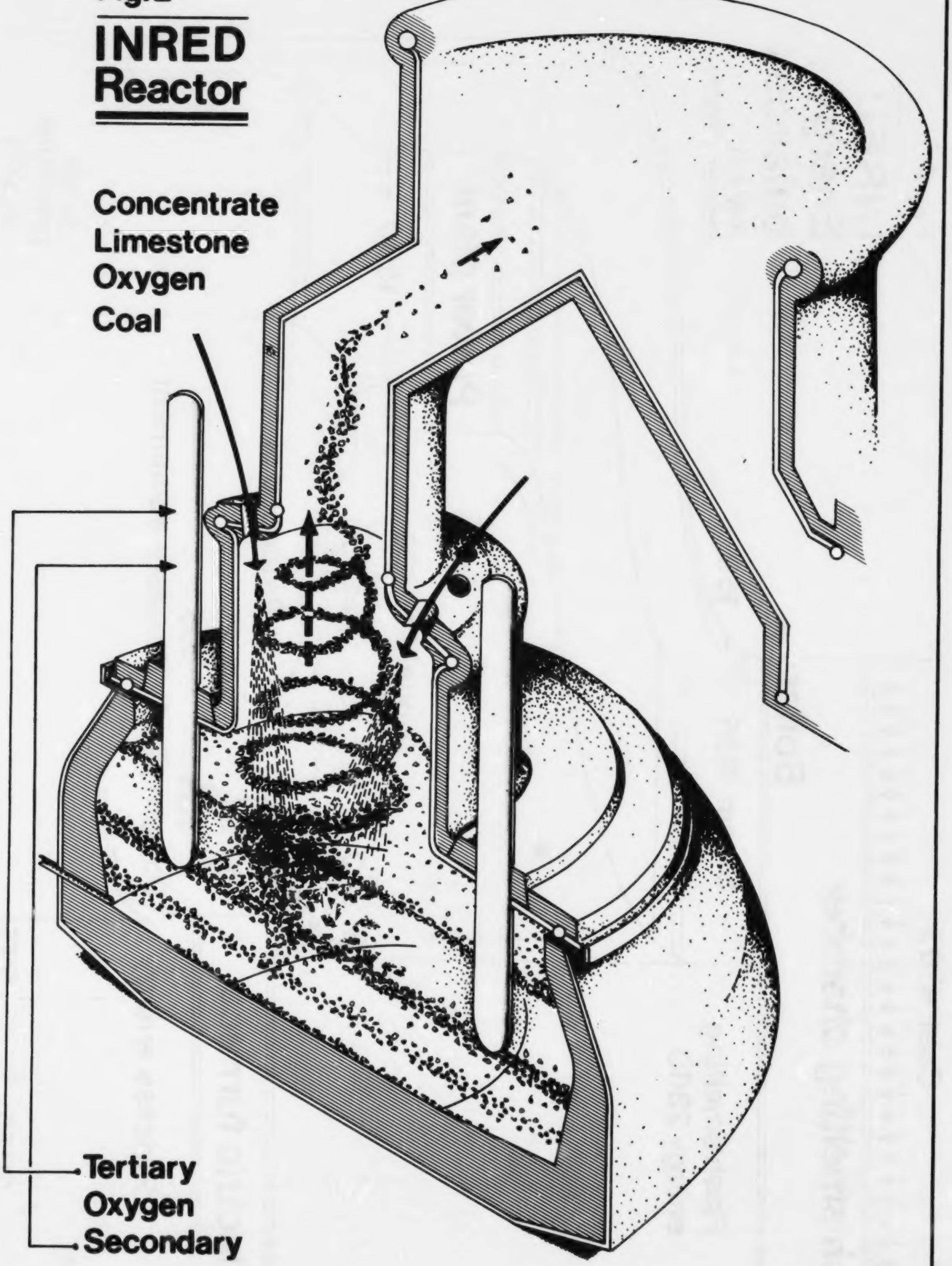

Oxygen plant
turbine
Generator
connection to grid
Oxygen
steam
El
Coal
concentrate
Flash smelting Prereduction 1900°c
El-smelting Final treatment 1450°c
hot metal
Waste gas
Slag

Fig. 2



INRED Reactor
Concentrate
Limestone
Oxygen
Coal
Tertiary
Oxygen
Secondary

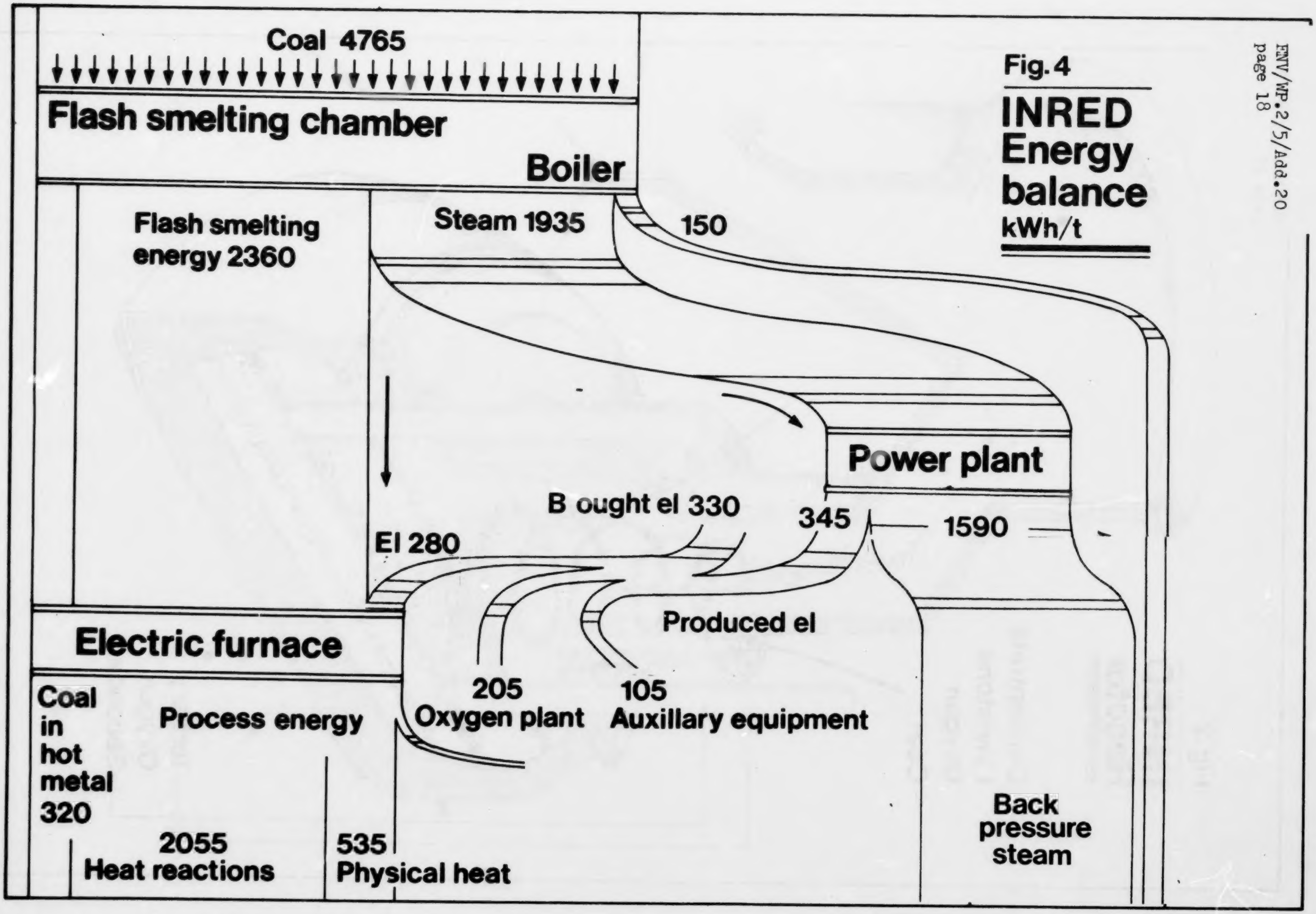


Fig. 4

INRED Energy balance

kWh/t

Coal 4765
Flash smelting chamber
Boiler
Flash smelting energy 2360
Steam 1935
150
Power plant
B ought el 330
345
1590
El 280
Electric furnace
Produced el
205
Oxygen plant
105
Auxillary equipment
Coal in hot metal 320
Process energy
2055
Heat reactions
535
Physical heat
Back pressure steam